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THE
ABSORPTION SPECTRA OF SOLUTIONS

OF COMPARATIVELY RARE SALTS

INCLUDING THOSE OF GADOLINIUM, DYSPROSIUM, AND SAMARIUM
THE SPECTROPHOTOGRAPHY OF CERTAIN CHEMICAL REACTIONS
AND THE EFFECT OF HIGH TEMPERATURE ON THE ABSORPTION SPECTRA
OF NON-AQUEOUS SOLUTIONS

BY
HARRY C. JONES AND W. W. STRONG

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PREFACE.

The work recorded in this monograph on the absorption spectra of solutions is a continuation of that already published by Jones and Uhler (Publication No. 60, Carnegie Institution of Washington), Jones and Anderson (Publication No. 110, Carnegie Institution of Washington), and Jones and Strong (Publication No. 130, Carnegie Institution of Washington). This work, like that recorded in the preceding publications, has been made possible by grants awarded by the Carnegie Institution of Washington.

The attempt has been made in this work to solve three problems:

First, to map out the absorption spectra of certain comparatively rare substances. Urbain has generously forwarded Dr. Strong ample quantities of the oxides of gadolinium, dysprosium, and samarium with which to prepare their salts and study their spectra. We find that the salts of dysprosium and samarium have spectra that are almost as interesting as those of neodymium, with very sharp, characteristic bands.

Second. Under the spectrophotography of chemical reactions we have studied especially the effect of oxidizing agents on uranous salts. We have used milder oxidizing agents and stronger oxidizing agents, and have dissolved the uranous salt in single solvents and in mixed solvents. When uranous chloride is dissolved in a mixture of alcohol and water, both the "alcohol" and the "water" bands come out simultaneously on the plate. A mild oxidizing agent was found to oxidize the "hydrated" salts and to leave unaffected the "alcoholated" salts. A strong oxidizing agent, on the other hand, oxidized both the "hydrated" and the "alcoholated" uranous salt to the uranyl condition. This is, therefore, an example of "selective oxidation."

Third. By means of the closed cell we have been able to study the absorption spectra of solutions in methyl and ethyl alcohols up to temperatures as high as 195°. The absorption bands widen with rise in temperature up to the highest temperatures employed. Colored solutions, therefore, become more and more nearly opaque as the temperature to which the solutions are subjected is raised.

The effect of rise in temperature on the absorption spectra of neodymium salts in mixtures of alcohol and water, where both the "alcohol" and the "water" bands appear simultaneously, has been studied. The "water" bands are more affected by rise in temperature than the "alcohol" bands, showing that the "hydrates" are less stable with rise in temperature than the "alcoholates."

The problems now under investigation include the effect of ions as compared with molecules on the absorption spectra of solutions, the effect of high temperature on the absorption spectra of aqueous solutions, and the measurement of the intensity of the various absorption bands by means of the radiomicrometer and thermoelectric junctions.

It gives me special pleasure to express my indebtedness and thanks to the Carnegie Institution of Washington for the generous support which they have given this work in the past and for the aid which they have tendered for the future.

I wish to express my thanks to Professor J. S. Ames for ample space in the Physical Laboratory for carrying out the physical part of this work; to Professor J. A. Anderson for a large number of valuable suggestions in connection with the work; to Professor A. H. Pfund for advice in connection with the construction of the radiomicrometer; and to Dr. J. Sam Guy, who will continue this work, for aid especially in preparing the various salts and solutions of the salts of dysprosium and samarium.

HARRY C. JONES.

JUNE 1911.

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CHAPTER I.

THE ABSORPTION AND EMISSION CENTERS OF LIGHT AND HEAT.

During the last decade a considerable number of physicists have directed their efforts towards solving some of the many problems of spectroscopy. The following chapter will contain a discussion of some of this work, with the view of recording part of our experimental knowledge concerning the nature of the emission and absorption centers of light; the connection between these centers and molecular and atomic structures; the effect of ionization and recombination on these centers, and the effects and changes that can be produced by physical and chemical agents such as temperature, the presence of a magnetic field, etc., upon the constitution of the emission and absorption centers.

Emission and absorption centers will be defined as the smallest particles from which we can obtain characteristic absorption or emission spectra. A further division of the centers of any characteristic spectrum would make it impossible to obtain that spectrum, though the resultant particles may possess characteristic absorption or emission spectra of their own. When emission or absorption centers move with reference to an observer, the frequencies of the spectral lines and bands will show the Döppler effect.

ATOMIC STRUCTURE AND SPECTRA.

A very important problem is that of the relation between chemical constitution and absorption or emission spectra, although the relation between flame, spark, and arc spectra, and the chemistry of the absorption and emission centers may not be known. Even the source of spectra like that from the blue cone of a bunsen burner, the Swan spectra, is at present a much mooted question. It is probable that chemical reactions play an important rôle in emission and absorption spectra, and especially in band spectra. We usually think of most spectrum lines, like D_1 and D_2 of sodium, as coming from the metallic atoms. Fredenhagen points out that under most conditions oxygen is present. In chlorine, hydrogen, or fluorine flames, calcium, strontium, thallium, sodium, barium, and copper emit spectra that are very different from those obtained when oxygen is present. Under these conditions thallium does not emit the characteristic green line, and the lines D_1 and D_2 are completely absent. Work on the absorption of sodium, mercury, potassium, and various other vapors shows that the presence of foreign gases modifies the character of the absorption very much.

Chemical reactions and processes of ionization and recombination are believed to place the atom or molecule in a peculiar condition, in which it can emit energy to the ether or absorb energy from it. Under ordinary conditions the atom does not seem capable of doing this. In sodium vapor, for instance, according to present theories only one atom in thousands is taking part in absorption at any one time. The problem as to how energy is transferred to and from matter is one of the most fundamental problems of science. A striking example of the fact that a few atoms under peculiar conditions have the power of absorbing an enormous amount of energy is exhibited by the iron absorption lines in the solar spectrum. An arc of carbon electrodes containing iron as an impurity emits enough iron vapor to absorb as much as the iron vapor in the sun. It is thus seen that an infinitesimal amount of iron in the very great atmosphere of the sun is sufficient to absorb a large part of the energy emitted by the photosphere.

Our present theory of the mechanism of the absorption and emission of radiations is very simple. Light and heat are electromagnetic radiations, and hence the emission and absorption centers must contain either or both electric charges and magnetic poles. As free magnetic poles are unknown to us, while free electric charges are known, this theory makes the electric charge the origin of electromagnetic phenomena. At present no positive electric charges are known to be associated with portions of matter smaller than the hydrogen atom. On the other hand, negative electrons are known to be associated with masses only about one two-thousandth that of the hydrogen atom. As far as experiment shows, these electrons always have the same properties and the same charge (the charge is invariably considered as constant when e/m varies), no matter from what element they may come. It is for these reasons that the electron is made the fundamental unit in the electromagnetic theory.[1]

Electromagnetic radiations, then, have their origin in electric charges. Continuous spectra (as from hot metals) are due to free electrons, and these apparently have very little connection with the chemical constitution of the metal molecules. Fine line and band spectra are apparently due to different systems of electrons within the atom, and are greatly affected in intensity by the presence of neighboring atoms. The electrons of this type vibrate in definite frequencies that can be changed only very slightly by changing the external conditions.

THE IONIZATION THEORY AND ABSORPTION AND EMISSION CENTERS.

Several investigators have considered that band spectra are due to vibrations in some way peculiar to a condition existing during the dissociation of molecules or the recombination of the dissociated parts. According to Koenigsberger and Kupferer[2] the band spectra of iodine, bromine, nitrogen dioxide, sulphur, iodine trichloride, and probably nitrogen and the other gases are due to a dissociation of this kind. Iodine is a typical example. At 60° C. and about 4 mm. pressure the reaction, as expressed by them, is as follows:

$$I_2 \rightleftarrows I + I$$

At about 800° C. this reaction is practically complete. According to them, iodine possesses a continuous absorption which has a maximum in the green, and this continuous absorption decreases with rising temperature. At 600° and above, the absorption is almost entirely in the violet and ultra-violet and is due to the iodine atom. The banded absorption, consisting of thousands of fine lines, results whenever chemical reactions represented by the above equation take place. During these reactions it is possible that the atoms may exist in the so-called "nascent" condition, and their electrons may then be subjected to very little, if any, damping. In such reactions it might be expected that the gas would be greatly ionized. This, however, is not the case, as was shown by Henry[1] and Whiddington.[2]

---

[1] Phys. Zeit., 8, 729 (1907). [2] Ibid., 11, 568 (1910).

Several workers, including Galitzin and Wilip,[3] have studied the absorption spectra of bromine at different temperatures and pressures. As the temperature is raised the fine band absorption spectrum changes, becomes more and more indistinct, and finally disappears at high temperatures. Evans[4] has shown that the temperature of the disappearance of the absorption bands is higher the greater the pressure. The disappearance of the absorption lines is closely connected with the dissociation of the diatomic bromine molecules, and the disappearance of absorption at high temperatures can be explained by assuming that the monatomic molecules have no absorption between λ 3500 and λ 6800.

Heated bromine and iodine vapors give an emission spectrum that coincides with the absorption banded spectrum. Evans believes that the absorption spectra disappear as soon as the emission due to the dissociation and recombination of the diatomic molecules is equal to the absorption of the undissociated state. Evans gives the following table:

Pressure of bromine vapor.	Temperature of disappearance of spectrum.	Fraction of dissociation.	Fraction of dissociation observed by spectroscope.
mm.	°*C.*		
24	950	0.22	0.25
35	1030	.37	.39
49	1090	.49	.51
63	1136	.58	.58
88	1220	.74	.68
160	1320	.84	.79
246	(1)	....	(2)

[1] Spectrum still present at 1320° C.
[2] Tube becomes opaque, collapsing at 1400° C.

SULPHUR BANDS.

Graham[5] has investigated the absorption spectra of sulphur vapor between 530° and 900° C., the pressure being in general about 10 mm. of mercury. Above 580° C. the dissociation is considered to be from S_8 to S_2. At or below 520° C., Graham believes that there are intermediate compounds formed between S_8 and S_2. The following are the wave-lengths of some of the sulphur bands:

---

[1] Proc. Camb. Phil. Soc., **9**, 319 (1897).
[2] *Ibid.*, **15**, 189 (1909).
[3] Mémoires de l'Académie des Sciences de St.-Petersbourg, **17**, 1–112 (1906).
[4] Astrophys. Journ., **32**, 281 (1910).
[5] Proc. Roy. Soc., A, **84**, 311 (1910).

S_1		S_2		
4775	4245	3415	3060	2805
4705	4195	3365	3025	2770
4645	4150	3330	2990	2745
4580	4100	3290	2960	2715
4530	4050	3255	2930	2690
4465	4005	3215	2900	2665
4405	3985	3170	2860	2640
4350		3130	2835	2620
4290		3095		

The question as to whether the fluorescence of a gas or liquid influences its conductivity has in general been answered in the negative. Nichols and Merritt[1] reported that the conductivity of an alcoholic solution of eosin was increased when the solution was caused to fluoresce. Carmichel[2] and Regner[3] found no such effect, while Hodge[4] and Goldman[5] have shown that the effect found by Nichols and Merritt was due to an electromotive force produced by the light at the electrodes of the cell. Howe[6] finds that if the fluorescence of anthracene increases the conductivity, the increase is too small to measure. Wood could detect no increase in the conductivity of sodium vapor when it was caused to fluoresce.

On the other hand, Nichols and Merritt[7] believe that in the case of the fluorescence of solutions of fluoresceïn, the emission center may be the ion, although they have examined the effect of change of concentration upon the absorption spectrum of eosin and find very little effect. The absorption curve is steep towards the red, and gradual towards the violet. The fluorescent curve slopes in the opposite manner. Their work indicates that the molecules and ions seem to behave in much the same way in absorption phenomena. The same writers[8] have investigated the problem as to whether the fluorescence excited per unit of absorbed energy is constant for all wave-lengths. Confining the range of absorption to that of a single band, they conclude that the light near the red side of the band is more effective in producing fluorescence than that lying on the violet side; and the change in specific exciting power in passing along the band is continuous, without any indication of anything selective in the neighborhood of the region of maximum absorption.

THE CARRIERS OF CANAL-RAY SPECTRA.

A large number of investigations have been made on the spectra produced by canal rays. In the earlier work Stark was of the opinion that the renewal of energy to a vibrating atom took place at the moment of collision between the radiating atom and some other moving part; and the smaller the mass of the particle collided with, the more efficient it would be in exciting vibrations inside the atom, since the velocity of the small particle is greater and the time occupied by a collision would be shorter. Continuous radiation of energy by an atom moving with a comparatively small velocity would only be made possible, then, by its frequent collisions with free electrons. On the other hand, band spectra, which are not in general affected by electric fields, Stark considers as being due to the combining of a positive ion and a negative electron. During this recombination there is a considerable decrease in the potential energy of the system, and it is from this energy that the band spectrum is produced.

---

[1] Phys. Rev., **19**, 296 (1904).

[2] Jour. de Phys., 4, 873 (1905).

[3] Phys. Zeit., 4, 862 (1903).

[4] *Ibid.*, **28**, 25 (1908).

[5] Ann. d. Phys., **27**, 332 (1908).

[6] Phys. Rev., **30**, 453 (1910).

[7] *Ibid.*, **31**, 376 (1910).

[8] *Ibid.*, 381 (1910).

In their early work Stark and Riecke[1] describe an arc-like discharge between copper electrodes of about 3600 volts difference in potential. The vapors of sodium or lithium salts placed in this discharge spread towards the negative wire, thus indicating that the carriers are positive; this being a direct contradiction of Lenard's results.

Most of Stark's later work has been done with canal rays. They move towards the cathode and pass through any openings in it, with a velocity of about 10^8 cm. per second. If there is hydrogen in the tube both the line and band spectra of hydrogen may be seen. In nitrogen the line spectra are difficult to obtain. The lines of hydrogen, nitrogen, mercury, sodium, potassium, etc., are found to show the Döppler effect when viewed in the direction in which the canal-ray particles are moving.

The substances showing the Döppler effect also give spectra that do not show the Döppler effect, *i.e.*, there are rest lines and shifted lines. The rest line is usually much the sharper of the two, and the space between the two lines is usually dark. The line shifted towards the violet usually has its sharpest side on the red. The rest line comes largely from the gas through which the canal rays are passing. The displaced line is composed of light radiated by the canal-ray particles themselves, and since these lines are hazy, the canal rays are moving with different velocities, according to the part of the "cathode fall" region from which the particles originate. The particles that traverse the whole region of the cathode fall will accordingly have the maximum velocity. Having passed through a field of from 300 to 500 volts, the velocity of the canal-ray particles becomes sufficient to produce ionization by collision.

Knowing the cathode fall, the mass of the canal particle, and the maximum displacement, Stark calculates the charge of the canal particle. For the hydrogen series, the principal and subordinate series of sodium and potassium, and for certain lines of mercury, the value of the charge, according to the earlier papers of Stark, is the same as that of the elementary charge of electricity. Stark also considered the mercury triplets to be due to particles carrying a double charge, and the mercury line λ 4078.1 to be due to a carrier having more than two charges.

THE CARRIERS OF SPARK SPECTRA.

Among investigators who have taken up the problem as to what is the nature and velocity of the particles in sparks that are acting as absorption and emission centers of line spectra, may be included Schuster and Hemsalech,[2] Schenck,[3] Royds,[4] Milner,[5] Miss Schaeffer,[6] and others. These workers have studied the velocity of the light streamers, and in some instances have found indications that the emitting centers carried a negative charge. The subject is such a complicated one, however, that it must be stated that our knowledge at present concerning the constitution of these emission centers is extremely meager.

---

[1] Phys. Zeit., **5**, 537 (1904).

[2] Phil. Trans., **193**, 203 (1900); Compt. Rend., **142**, 1511 (1906).

[3] Astrophys. Journ., **14**, 116 (1901).

[4] Phil. Trans., **208**, A, 333 (1908).

[5] *Ibid.*, **209**, 71 (1908).

[6] Astrophys. Journ., **28**, 121 (1908).

THE EMISSION CENTERS OF FLAMES AND ARCS.

The study of the Zeeman effect has shown beyond a doubt that the vibrations of the emitting centers of many arc, spark, and flame lines are affected by an outside magnetic field, in the same way as negative electrons would be affected; and it is remarkable how closely the value of e/m, as calculated from the Zeeman effect, agrees with the value as found for the cathode and β-ray particles. The Zeeman effect does not, however, give us much knowledge of the radiating centers, since the electrons form only a small part of these centers.

A very important series of experiments has been carried out by Lenard[1] and others. The main conclusion from this work was that the carriers of the first subordinate series in the Kayser and Runge classification of spectrum lines are positively charged ions. The reason that ions in liquids do not radiate, Lenard explains as due to their being loaded down by neutral molecules. The work of other investigators has made this conclusion very doubtful, so that, as in the case of spark and canal-ray spectra, it must be concluded that at present nothing is known with certainty as to what the constitution of the radiating centers may be.

SCHUMANN WAVES.

In 1893 Schumann studied the extremely short ultra-violet wave-lengths to about λ 1200. Lyman[2], by using a concave grating, has studied the spectra of hydrogen from λ 2000 to λ 1030, there being no radiations apparently between λ 3000 and λ 1700. Argon possesses a rich emission spectrum in this region. The spectra of carbon monoxide and dioxide seem to be very much alike, and produce radiations to λ 1300. Oxygen and nitrogen do not seem to emit in this region. Fluorite is the only substance transparent to λ 1225. Quartz 0.5 mm. thick absorbs everything beyond λ 1500. Argon, helium, hydrogen, and nitrogen in a layer of 1 cm. are perfectly transparent. The absorption of air is due to the presence of oxygen. Oxygen of 9 mm. depth and 380 mm. of mercury pressure has an absorption band extending from λ 1750 to λ 1275.

THE POSSIBLE CATALYTIC ACTION OF LIGHT.

Weigert[3] has worked upon the equilibrium of the gas $COCl_2$ and its products, $CO + Cl_2$. The reaction

$$CO + Cl_2 = COCl_2$$

is accelerated by the action of light, but the position of the final equilibrium is unaffected by the action of the light, and is a function only of the temperature. The light thus acts as a catalyzer and not as a source of energy.

---

[1] Ann. d. Phys., 9, 642 (1902); 11, 649 (1903); 12, 175 (1903); 12, 737 (1903); 17, 197 (1905).

[2] *Ibid.*, 77, [illegible]

[3] Le Radium, 4, [illegible] (1907); Ann. d. Phys., 24, 243 (1907).

Weigert believes that there are formed molecular complexes or "reaction nuclei" by the light, analogous to the ions formed by ultra-violet light in air; and these "reaction nuclei" play the rôle of a catalyzer, the reaction being produced with very great velocity on the surfaces of these nuclei, and the speed of the reaction will then be a function of the rate of diffusion of these nuclei.

Weigert finds that these "reaction nuclei" act as nuclei for the condensation, and thus supports the views of Burgess and Chapman.[1] When the light has produced a number of the "reaction nuclei," it is found that the number of these decay like ordinary ions. The "reaction nuclei" also accelerate the following reactions:

(1) Dissociation of oxychloride of carbon.
(2) Oxidization of hydrogen.
(3) Oxidization of sulphurous acid.
(4) Decomposition of ozone.
(5) Oxidization of hydrochloric acid gas.
(6) Formation of ammonia.

EMISSION SPECTRA OF ORGANIC COMPOUNDS.

Goldstein[2] has shown that bright, fluorescent, and phosphorescent light is emitted by solid aromatic compounds. The stimulation is best produced by cathode-ray bombardment. To prevent the evaporation of the compounds, they are kept cooled by liquid air. Goldstein has investigated a large number of organic compounds such as benzene, the three xylenes, benzonitrile, the quinolines, acetophenone, etc. In many cases three spectra appear which Goldstein calls the initial, the chief, and the solution spectra.

During the first moments of excitation the initial emission spectrum is quite strong, but it soon becomes very weak without disappearing. At the same time that the initial spectrum begins to diminish in intensity the chief spectrum appears. This spectrum is a very characteristic one, even for isomeric compounds. The third type of spectra only appears when an aromatic compound is dissolved in a liquid and the solidified solution is exposed to cathode rays.

The chief spectrum consists largely of narrow channeled bands, which usually have their sharper edges on the short wave-length side. These spectra never have bands of shorter wave-length than λ 4600. The initial spectra extend much farther than this into the region of short waves.

Chief Spectrum of Naphthalene.

λ 5390 (very bright)	5890 (very bright)
5550	6150 (probably double
5600	6300
5730	6480

Spectrum of Naphthalene in Monochlorbenzene.

λ 4730 bright	5050	5170 faint	5400 faint	5570 faint	5820 faint
4830 "	5100	5230 "	5450 "	5650 "	

The solution spectrum varies greatly for different solvents, even for isomeric compounds.

---

[1] Trans. Chem. Soc., 89, 1423 (1906).
[2] Verhandl. d. deutsch. Ges., vi, 156, 185 (1904); Phil. Mag., 20, 619 (1910).

The phosphorescence of several organic compounds has been studied by Kowalski.[1] Phosphorescence was found to appear in many cases at about −150° C., depending on the substance dissolved in the alcohol. When phosphorescence first appears it only lasts a few hundredths of a second, but as the temperature is lowered the duration of the phosphorescent light increases very appreciably. If the time of excitation is short, an "instantaneous" phosphorescence results which resembles the fluorescence of the solution. If the time of excitation is increased, fine bands are superimposed upon the broad fluorescent bands, and these increase in intensity as the time of excitation is increased. The time required to reach a maximum intensity is different for different bands. The duration of these bands is much longer than that of the "instantaneous" phosphorescence, and is called by Kowalski "progressive phosphorescence."

Kowalski and Dzierzbicki give the following wave-lengths for the progressive phosphorescent bands in ethyl alcohol:

(1) Benzene, 0.05 normal solution in alcohol: λλ 3390, 3460, 3520, 3570, 3650, 3710, 3800, 3850, 3970, 4020, 4130, 4190, 4290, 4350.

(2) Toluene, ethylbenzene, and propylbenzene, 0.05 normal solution in alcohol. The introduction of the methyl group into the benzene nucleus transforms the 14 benzene doublets into 7 broad bands, occupying almost the same position in the spectrum. An introduction of a methyl group in a side chain produces very little effect. The toluene bands are at λλ 3460, 3580, 3650, 3800, 3890, 4060, and 4120. The ethylbenzene bands are at λλ 3450, 3580, 3640, 3780; 3870, 4050, and 4120. The propylbenzene bands are at λλ 3440, 3580, 3650, 3790, 3890, 4050, and 4130.

(3) The bands of a 0.05 normal solution of *o*-xylene, $C_6H_4(CH_3)_2$, are at λλ 3480, 3560, 3610, 3670, 3780, 3830, 3900, 4000, 4070, and 4130; *m*-xylene, $C_6H_4(CH_3)_2$, at 3540, 3610, 3670, 3730, 3820, 3880, 3970, 4090, 4160, and 4230; and *p*-xylene, $C_6H_4(CH_3)_2$, at 3550, 3650, 3700, 3770, 3890, 3950, 4010, 4120, 4190, and 4270.

(4) Pseudocumene, mesitylene, and cymene all show bands at λλ 3560, 3650, 3770, 3880, 4000, 4120, and 4270.

(5) Phenol shows bands at λλ 3510, 3610, 3710, 3830, 3960, and 4080.

(6) *o*-cresole has bands at λλ 3530, 3630, 3740, 3850, and 3970; *m*-cresole at 3540, 3620, 3730, 3850, 3970, and 4080; *p*-cresole at 3630, 3730, 3850, 3980, and 4110.

THE ABSORPTION SPECTRA OF ORGANIC COMPOUNDS.

The Unit of the Absorption.

In discussions concerning the color of organic compounds it is customary to speak of the selective absorption as being due to certain ions or molecules. This is probably true in the infra-red, the electric charges absorbing these long wave-length radiations being probably associated with masses of molecular size. However, in the visible and ultra-violet portions of the spectrum the value e/m of the absorbers is invariably of the same magnitude as that of the electron. Drude[2] has investigated a large number of organic compounds, and shows that the absorber of all the shorter waves of the spectrum is the negative electron.

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[1] Compt. Rend., 151, 810 (1910).

[2] Ann. d. Phys., 14, 677, 726, 936, 961 (1904).

Throughout this part of the present monograph the absorbers are considered as negative electrons. These electrons have certain free periods corresponding to the bands of selective absorption. These free periods are greatly modified by the presence of certain chemical radicals, and seem to be electrons that are situated either in the outer parts of the atom or between two or more atoms. Stark and others call these the valency electrons, and consider that chemical valency is due to them. Chemical bonds will then be closely associated with the electric fields of these electrons. While the theory in its present state is confronted with many difficulties, yet it seems a step towards the explanation of the more or less vague chemical bond. As an aid to our imagination, we shall consider atoms or ions as large spherical regions throughout which a positive charge is uniformly distributed. These regions are sometimes spoken of as "spheres of influence." Two atoms collide when their "spheres of influence" touch. Groups of atoms composing ions, radicals, or molecules will have "spheres of influence." No ion can penetrate the sphere of influence of another atom or molecule. On the other hand, the electrons are very small and bear much the same relations in size to the atom that the sun bears to the solar system. The electric fields of the electrons, however, occupy quite large volumes, although the energy of this field is for the most part situated in a very small space. Electrons can, therefore, move through ions and atoms if they have sufficient velocity. In most organic compounds it is considered that the valency electrons move in the interatomic spaces with considerable ease. In the metals a large number of the electrons are free. In organic compounds that are transparent to certain wave-lengths, the electrons in general will be held within certain regions by forces that are supposed to be elastic in their nature.

A considerable amount of work has been done by Koenigsberger and Kichling[1] on the determination of the coefficients of absorption of organic coloring matters, compounds of the metalloids, minerals, etc. Selective absorption is classified under two heads. In the first class the absorbing and reflecting powers are closely connected, and the absorption is probably due to electrons or ions vibrating in the chemical molecule; in the second class the absorption has no effect on the reflecting power, and the absorbers in this case are rare and are not connected with the molecular structure.

Letting p be the number of electrons per molecule, it is found that absorption curves give the value of $p\ e/m$ better than the dispersion curves. For organic coloring matters $p\ e/m = 1.3(10)^7$. For a temperature of absolute zero, they consider that $p\ e/m = 1.78(10)^7$. This quantity decreases as the temperature rises to the probable limit $\frac{1}{2}\ 1.78(10)^7$. For the metalloids there is a single vibrating electron for the bromine family of elements, two for the selenium family, and three for the phosphorus family.

For a large number of substances, the absorption curve is displaced towards the red when the temperature is raised. It widens and becomes flatter at the same time. From this it seems that the quasi-elastic force that acts on the electron decreases with rise in temperature.

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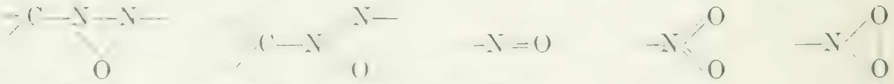
[1] Ann. d. Phys., 28, 889 (1909); 32, 843 (1910); Phys. Zeit., 12, 1 (1911).

THE THEORY OF CHROMOPHORES.

In considering absorption spectra it is often quite sufficient to speak qualitatively of the color of different compounds. The introduction of certain groups into colorless compounds often results in a colored compound. Any such group is a chromophore. Sometimes the chromophore may be weak, and it may require the addition of several chromophores to produce a colored compound. Ultimately the color is due to absorbers existing in the chromophore, probably the valency electrons. Among the better known chromophores are the groups:

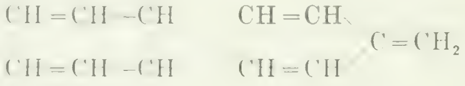
$>C=C<$ $=CO$ $>C=NH,$ $-CH=N-$ $-N=N-$



$$>C-N-N- \quad >C-N\begin{matrix}N-\\O\end{matrix} \quad -N=O \quad -N\begin{matrix}O\\O\end{matrix} \quad -N\begin{matrix}O\\O\end{matrix}$$

$=N=O$ $=C=S$ $-C-S_2-C-.$

The ethylene group, $>C=C<$, is a weak chromophore, and several chromophores must be present before the absorption is sufficient to produce color. An example is that of benzene and its isomer:



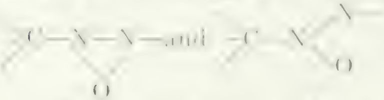
$$\begin{matrix}CH=CH-CH\\CH=CH-CH\end{matrix} \qquad \begin{matrix}CH=CH\\CH=CH\end{matrix}>C=CH_2$$

Benzene. Isomer.

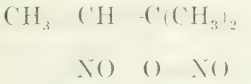
Benzene is colorless and exhibits absorption only in the ultra-violet, whereas the isomeric compound is orange yellow.

The carbonyl group, $=C=O$, is also weak, and several of the groups must be present in a compound to produce color. The following examples indicate how an increasing number of the carbonyl groups produces a greater and greater absorption of the shorter wave-lengths:

$R-CO-R$, colorless.
$CH_3-CO-CO-CH_3$, yellow.
$C_6H_5-CO-CO-C_6H_5$, yellow.
$CH_3-CO-CO-CO-CH_3$, orange.
$C_6H_5-CO-CO-CO-CO-C_6H_5$, red.

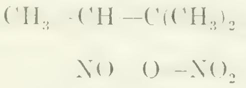
The combination of two phenyl groups causes absorption only in the ultra-violet. The introduction of the $-CH=N-$ chromophore is sufficient to produce color, as is shown in the yellow benzylidenaniline, $C_6H_5CH=N-C_6H_5$. The azochromophore, $-N=N-$, produces the same effect, as shown in the orange azobenzene, $C_6H_5-N=N-C_6H_5$. The chromophores  $>C-N-N-$ and $>C-N\begin{matrix}N-\\O\end{matrix}$, on the other hand, are very weak.

The nitroso group, $-N=O$, is a very strong chromophore when it is joined to a carbon atom directly. The effect of this chromophore is shown in nitrosobenzene, $ON-C_6H_5$, which is green. Wallach,[1] and recently J. Schmidt,[2] have investigated the following compounds, which are of a deep blue color:



$CH_3-\underset{NO}{CH}-\underset{O-NO}{C}(CH_3)_2$

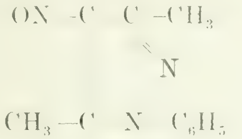
Alkylenenitrosite.



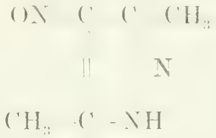
$CH_3-\underset{NO}{CH}-\underset{O-NO_2}{C}(CH_3)_2$

Alkylenenitrosate.

According to Wolff,[3] the following nitroso compounds, the first of which is green and the second blue, have the structures:

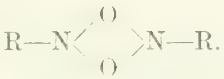


1-phenyl-3.5-dimethyl-4-nitrosopyrazol.



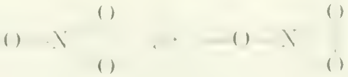
3-5-dimethyl-4-nitrosopyrazol.

The carrier of the color in these cases is the $C-N=O$ group. Many of the aliphatic nitroso compounds show polymerization and are then often colorless. The polymerization of $R-N=O$ to $(RNO)_2$ is probably accompanied by a rearrangement as follows:



This would explain why the polymer is colorless.

An application of the theory of isodynamic isomerism has been made by K. Schaefer[4] to the absorption of the NO_3 group. An exhaustive study has been made of the absorption of alkyl and metallic nitrates. In every nitrate investigated, the characteristic ultra-violet absorption was detected, and in general Beer's law was found to hold. It would be interesting to know whether the presence of other salts, acids, or solvents would change the NO_3 absorption. Schaefer finds for pure neutral solutions of inorganic salts that the absorption is independent of the metal. The absorption band appears to be independent of the ionization, since in the case of potassium nitrate the absorption is the same for the solid as for the concentrated and dilute aqueous solutions. The absorption is suggested to be due to the following oscillation:



The character of the absorption is similar for metallic and many organic salts. Methyl, ethyl, amyl, and allyl nitrates, however, show only general absorption. There was no evidence here of selective absorption, either in the liquid, vapor, or dissolved condition of the salts.

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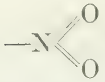
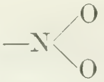
[1] Lieb. Ann., **241**, 288 (1887); **322**, 305 (1902).

[2] Ber. d. chem. Ges., **35**, 2323, 3721 (1902); **36**, 1768 (1903).

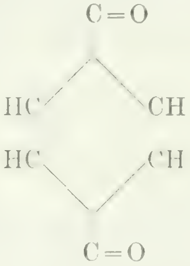
[3] Lieb. Ann., **325**, 192 (1902).

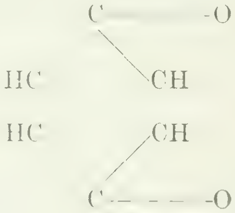
[4] Zeit. wiss. Phot., **8**, 212-234 and 257-287 (1910).

The nitro group  $—N\langle^{O}_{O}$ or  $—N\langle^{O}_{O}$ is a very weak chromophore. The aliphatic nitro compounds, CH_3NO_2, $C_2H_5NO_2$, etc., are colorless. When combined with other chromophores, colored compounds, such as nitrobenzene or nitronaphthalene, can be obtained. Stobbe[1] has investigated the influence of the nitro group on the fulgides. In solution the *p*-nitrophenylfulgide has a deep red color. The ortho and meta compounds are much less deeply colored.

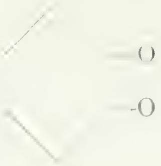
Hantzsch[2] and Raschig[3] have shown that the $=N=O$ group acts as a chromophore in the sulphonate, $O=N=(SO_3K)_2$, which is violet in solution and orange in the solid state. The thiocarbonyl group, $=C=S$, is a rather strong chromophore. Examples are the blue compounds thioacetophenone, $C_6H_5—CS—CH_3$, and thiobenzophenone, $C_6H_5—CS—C_6H_5$. For a fuller account of the color properties of various compounds, the reader is referred to Ley's paper,[4] from which the data here recorded have been largely taken.

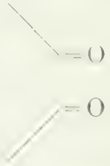
There has been a great deal of discussion whether quinone has the formula I or II:


I.


II.

Willstätter and F. Müller[5] have found that *o*-benzoquinone can exist in two forms, I and II, the former being colorless and the latter red:


I.


II.

This fact may possibly explain several outstanding difficulties among quinone derivatives. It would be expected that the substitution of an (NR) group for oxygen in a quinone would give a deeply colored substance. As a matter of fact, quinonediphenylimide,

$$C_6H_5N=C_6H_4=NC_6H_5$$

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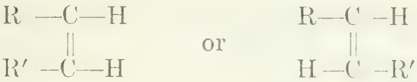
[1] Ber. d. chem. Ges., 38, 4082 (1905).
[2] *Ibid.*, 28, 2744 (1895).
[3] Dammer Handb. d. anorg. Chem.
[4] Jahrb. d. Rad. u. Elek., 6, 274–381 (1909).
[5] Ber. d. chem. Ges., 41, 2580 (1908).

is brownish red. But the compounds $NH : C_6H_4 : NH$ and $O : C_6H_4 : NH$ are colorless. This can easily be explained if the latter compounds are assumed to have the superoxide formula similar to that of *o*-benzoquinone. The quinone chromophore enters into the composition of quite a large number of colored compounds.

The space relations of the chromophores seem to affect the color of compounds. For instance, the ethylene group can have two isomeric configurations:



$$\begin{array}{c} R—C—H \\ \| \\ R'—C—H \end{array} \quad \text{or} \quad \begin{array}{c} R—C—H \\ \| \\ H—C—R' \end{array}$$

This geometric isomerism may explain the following facts:

1. Diethoxynaphthostilbenes, $C_2H_5O—C_{10}H_6.CH : CH.C_{10}H_6.OC_2H_5$.[1] The form which has the highest melting-point is colorless, while the lower melting form is yellow.

2. Dibenzoylethylenes, $C_6H_5CO.CH : CH.COC_6H_5$.[2] The higher melting form is colorless, while the lower melting form possesses a deep yellow color.

That the color-producing power of the chromophores is due to the double bonds seems quite certain. When these bonds are saturated the resulting compounds are colorless.

Colored.	Colorless.
$C_6H_5.CO.CO.CO.C_6H_5$, diphenyltriketone.	$C_6H_5.CO.CH_2.CO.C_6H_5$, dibenzoylmethane.
$C_6H_5—N=N—C_6H_5$, azobenzene.	$C_6H_5NH—NHC_6H_5$, hydrazobenzene.
$C_6H_5—N=O$, nitrosobenzene.	$C_6H_5—N.H.OH$, phenylhydroxylamine.
$O=C_6H_4=O$, quinone.	$HO.C_6H_4.OH$, hydroquinone.

The different di- and tri-substitution products usually give rise to different absorption bands when the absorption is selective. Ortho- and metaxylene have one band, whereas paraxylene has two. The following gives the value of the limit of absorption when light is passed through a gram molecule of the substance:

	Cresol.	Dihydroxy-benzene.	Hydroxy-benzoic acid.
Meta	3433	3466	3359
Ortho	3413	3399	3080
Para	3359	3151	2986

When a chromophore is introduced into a compound the bands may be shifted towards the red or towards the violet. The former effect is bathochromous, the latter hypsochromous. The effect of joining chromophores is usually bathochromous. For example:

	λ	λ	λ	λ
Benzene	2610	2540	2450	2440
Naphthalene	2850	2720	2630	2550
Anthracene	....	3600	3430	3280

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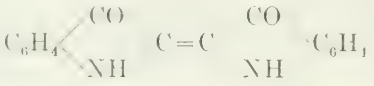
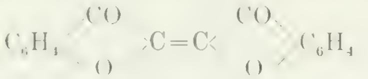
[1] Elbs: Journ. prakt. Chem., **47**, 72 (1893).

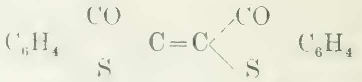
[2] Paal and Schulze: Ber. d. chem. Ges., **33**, 3795 (1900); **35**, 168 (1902).

In triphenylmethane the limit of the visible portion of the spectrum is reached. It may be stated that anthracene and phenanthrene have entirely different absorption spectra, although the fluorescent spectra are very similar.[1] An auxochrome is a radical that causes the absorption to be more intense. An example is —CO—C=C—CO—, which appears in the indigos,



and also in the deeply colored compounds





The groups CH_3, OCH_3, C_2H_5, the halogens, etc., are bathochromes, while the groups NO_2 and NH_2 are hypsochromes.

The infra-red absorption spectra to about 15μ of a large number of organic compounds have been investigated by Julius[2] and by Coblentz.[3] Isomeric compounds are found to possess very different absorption, depending on the combinations of the atoms in the molecule. Stereomeric compounds, on the other hand, were found to possess the same absorption spectra. The replacing of hydrogen by an NH_2 or CH_3 group usually results in the appearance of new bands. In the spectrum of certain benzene derivatives, however, the benzene spectrum is usually present. The carbohydrates investigated had characteristic spectra with absorption bands at 0.83 to 0.86μ; 1.67 to 1.72μ; 3.25 to 3.43μ; 6.75 to 6.86μ; and 13.6 to 14μ. The three isomeric xylenes have banded spectra in which the most important line in each group lies farthest toward the long wave-lengths in the order ortho, meta, and para.

Considerable work has recently been done by Weniger[4] upon the absorption of organic compounds in the infra-red. He finds that the alcohols have bands at 3.0 and 6.9μ; that changes from the primary to the iso-compounds cause small shifts; and that the secondary alcohols have a band at 7.6μ and the tertiary alcohols a corresponding one at 7.9μ. The band 9.6μ in the primary alcohols is shifted to 9.1μ in the secondary alcohols and 8.6μ in the tertiary alcohols. There are two minor bands in the primary alcohols which appear as follows:

Methyl.	Ethyl.	Propyl.	Butyl.
3.0μ	3.0	3.0	3.0
		3.5	3.5
4.9	5.2	5.5	5.6
5.9	6.0	6.1	6.1
9.9	9.6	9.6	9.6
	10.6	10.4	10.1
13.3	13.0	13.0	13.0

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[1] Elston: Astrophys. Journ., 25, 3 (1907).

[2] Verh. Konikl. Akad., Amsterdam, 1, No. 1 (1892).

[3] Investigation of Infra-red Spectra, Carnegie Institution of Washington Publication No. 35, by W. W. Coblentz.

[4] Phys. Rev., 31, 388 (1910).

It is seen that the shifts are towards the 9μ region of the spectrum. For the secondary alcohols Weniger gives the following:

Propyl.	Butyl.	Capryl.
7.2	7.3	7.3
9.0	9.1	9.1
9.9	9.8	9.4

In the case of primary acids Coblentz and Weniger give the positions of the following minima:

Acetic...........	3.5μ	5.9	7.2	8.9	9.9	10.6	11.0	13.9
Butyric.........	2.6	5.9	7.1	7.9	9.3	10.6	12.9	....
Valeric.........	3.6	5.9	7.1	7.9	9.1	10.7	12.2	13.3
Caproic.........	3.5	5.9	7.0	8.0	9.1	10.8	11.6	12.5
Stearic.........	3.5	5.9	7.0	7.8	9.2	10.6	12.2	13.3
Cerotic.........	3.5	5.9	6.9	7.7	...	10.6	10.9	12.9

Weniger considers the 3.0 and $6.9\mu\mu$ bands in the alcohols to be related to the hydroxyl group; the 3.4μ band in the alcohol, acids, and esters to be related to methylene (CH_2); the 7.3μ band in the esters and higher alcohols to be also related to methylene; and the bands 5.9μ and 8.2μ in all substances for which there are data to carbon monoxide.

The 9.6μ band in the primary alcohols shifts by 0.5μ to the violet when the linking of the hydroxyl is changed to secondary, and 0.5μ further changes when the tertiary alcohol is formed. The change from the primary to the secondary linking of the carboxyl group (CH_2COOH to $CHCOOH$) causes the doubling of a band in the 8μ region, this being true for acids and esters. The band of the carbonyl group is independent of the way in which this group is linked.

The authors[1] have shown that the effect of the NO_3 group and of free nitric acid is hypsochromous, causing the uranyl bands to shift towards the violet. The effect of free hydrochloric acid or of zinc, aluminium, or calcium chlorides on the uranyl chloride bands is bathochromous. Recently the authors have found that the NO_3 group is hypsochromous with respect to the neodymium and erbium bands.

Influence of the Solvent.

Theoretically it would be expected that the position of the absorption bands would be different for different solvents. Kundt's rule that the bands should be shifted to the red as the refractive index increases does not hold. It is usually believed that the application of Kundt's rule is obscured by the formation of compounds between the dissolved compound and the solvent. The formation of such solvates seems to be quite definitely proved for some inorganic compounds and organic solvents.[2] Kauffman, Hantzsch and Glover, Gorke, Koppe and Staiger, and others, have recently shown that the extinction coefficient varies somewhat for every solvent. In the same solvent the extinction coefficient usually increases as radicals are added to the dissolved substance, increasing its molecular weight. Hantzsch[1] furnishes evidence which shows the presence of solvates and molecular aggregates in the case of nitrohydroquinone dimethyl ether.

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[1] Phys. Rev., **28**, 143, **29**, 555 (1909); **30**, 279 (1910).

[2] Anderson: Phys. Rev., **26**, 520 (1908). Jones and Strong: Phys. Zeit., **10**, 499 (1909); Amer. Chem. Journ., **43**, 37, 97 (1910).

An interesting investigation has been made by Kalandek.[2] Resonators will emit electromagnetic waves of different wave-lengths, depending on the index of refraction of the liquid in which they are vibrating. Kalandek investigated the effect of different solvents on the period of various resonators, and also on the positions of the absorption bands of a large number of organic compounds. In general, the relations were not very close. It would be very interesting, however, to carry these investigations into the infra-red.

The Absorption Spectra of Benzene and Its Derivatives.

Benzene and several of its derivatives show selective absorption in the ultra-violet. Generally the absorption spectra of organic compounds consist of very wide, diffuse bands. The absorption bands of gaseous benzene, on the other hand, are very fine. Benzene in solution shows seven absorption bands between λ 2330 and λ 2710, and in the gaseous state about 30 bands. Pauer,[3] Friedrichs,[4] Grebe,[5] and Hartley[6] have investigated several of the benzene compounds. The bands in the gaseous state are much finer and usually more numerous than in solution or in the solid state.

Both the vapor and solution bands are shifted to the red when Cl, Br, CH_3, etc., are substituted for hydrogen. The shift is generally greater the greater the molecular weight of the radical. The bands of benzene shifted in this way are the ones that are common to benzene, toluene, ethylbenzene, and hydroxyxylene, and are unaffected by temperature and pressure. Hartley gives the following wave-lengths for benzene:

	λ	λ	λ	λ	λ	λ	λ
In solution........	2682	2657–2642	2614–2600	2539	2480	2426.5	2376
As vapor.........	2670	2630	2590	2523	2466	2411	2360

As far as investigated, the substitution products of benzene have much less characteristic spectra than the spectrum of benzene itself. It would be very interesting to know whether the shift of the bands is gradual as the state is changed or as different radicals are added.

Anthracene has the following bands:

	λ	λ	λ	λ	λ
Solid..............	4250	4495	4745	4980	5300
Solution...........	4050	4275	4540	4820	....
(Fluorescent) vapor	3900	4150	4320	....	....

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[1] Ber. d. chem. Ges., 40, 1556 (1907).

[2] Phys. Zeit. 9, 128 (1908).

[3] Wied. Ann., 61, 363 (1897).

[4] Z. wiss. Phot., 3, 154 (1905).

[5] *Ibid.* 3, 363 (1905).

[6] Journ. Chem. Soc., 77, 839 (1900). Phil. Trans., 208, A, 475–528 (1908).

The substitution of saturated groups in benzene has been found to change the absorption spectra but little. Unsaturated radicals like NH_2, COOH, etc., change the spectra very greatly, so that there is hardly any relation to the benzene spectra. In the various di-substitution products, the para compounds retain the characteristics of the benzene absorption better than the ortho or meta compounds. A considerable amount of work has been done by Hartley,[1] Baly and Desch,[2] Ley and von Engelhardt,[3] Baly and Collie,[4] Ley,[5] Hartley and Hedley,[6] Baly and Tuck;[7] and others have worked on the halogen, amino, and nitro compounds of benzene, the phenols, pyridine, and its substitution products. Below are a few of the results obtained.

Purvis[8] has studied the absorption spectra of the vapors of pyridine and some of its derivatives at different temperatures and pressures. Following are some of the bands:

Pyridine.	Pyridine.	Pyridine.	α-Picoline.	Piperidine.	Piperidine.
2930 n. wk.	2815 dif.	2747 wk.	2880 wk. sh.	2637 wk.	2535 st.
2918 n. wk.	2809 dif.	2743 wk.	2861 wk.	2633 wk.	2530 st.
2913 n. wk.	2806 wk.	2738 wk.	2859 wk.	2628 wk.	2528 wk.
2895 n. wk.	2798 wk. n.	2736 wk.	2856 wk.	2625 wk.	2526 wk.
2892 n. wk.	2796 wk.	2733 wk.	2846 wk.	2599 wk.	2521 wk.
2878 sh. wk.	2795 wk.	2730 st.	2834 wk.	2596 wk.	2519 st.
2869 sh. wk.	2789 st.	2726 st.	2821 wk.	2595 wk.	2513 st.
2866 sh. wk.	2784 wk. n.	2718 st.	2819 wk.	2591 wk.	2507 st.
2861 sh. wk.	2782 wk. n.	2713 st.	2814 wd.	2590 wk.	2503 st.
2859 sh. wk.	2778 wk. n.	2696 dif.	2809 wd.	2589 wk.	2502 wk.
2855 wk.	2762 wk. n.	2690 dif.	2790 n.	2586 wk.	2499 wk.
2849 wk.	2760 wk. n.	2685 dif.	2786 wd.	2579 sh.	2495 wk.
2843 wk.	2758 wk. n.	2678 wk.	2785 wd.	2565 wd.	2490 wk.
2832 sh. st.	2754 st.	2673 wk.	2781 wd.	2558 wd.	2472 wk.
2822 sh. wk.				2552 wk.	2467 wk.
				2550 wk.	2461 wd.
				2547 wk.	2455 wd.
				2543 wk.	2450 wd.
				2539 wk.	

n. = narrow; wk. = weak; sh. = sharp; st. = strong; dif. = diffuse; wd. = wide.

In the pyridine vapor spectrum it was found that the longer wave-length bands became wider and increased in intensity as the temperature and pressure were increased. In fact, all bands showed an increase in width and intensity under these conditions, and the general absorption in the ultra-violet was also greatly increased. The piperidine bands are wider and more diffuse than the pyridine bands. Some of the piperidine bands were coincident with the benzene bands. Benzene bands, however, have most of the sharp edges of the bands on the red side, whereas the piperidine bands are wider and are diffuse on both sides.

Hartley has shown that the vapors of *o*-, *m*-, and *p*-xylenes, 1-methyl-4-propylbenzene, and 1:3:5-trimethylbenzene have very few bands compared with benzene vapor, which has 82 bands. The same is true of pyridine vapor, in comparison with the much smaller number of bands of α-picoline and the disappearance of the bands in the lutidines and trimethylpyridine. The disappearance of the bands as the number of methyl groups in the pyridine ring increases is analogous to the lessened persistency of the absorption band as the number of methyl groups is increased when the substances are examined in alcoholic solution. No absorption bands are found for alcoholic solutions of piperidine.

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[1] Handbuch der Spectroscopie, vol. III.

[2] Journ. Chem. Soc., 93, 1345, 1747, 1902 (1908).

[3] Ber. d. chem. Ges., 41, 2990 (1908).

[4] Journ. Chem. Soc., 87, 1344 (1905).

[5] Ber. d. chem. Ges., 41, 1637 (1908).

[6] Journ. Chem. Soc., 91, 319 (1907).

[7] *Ibid.*, 93, 1902 (1908).

[8] Journ. Chem. Soc., 97, 692 (1910).

Vapors.			
Furane.	Furfuraldehyde.		Thiophene.
2652 weak.	2726 weak.	2681	2590 weak.
2647 "	2725 "	2679	2530 "
2642 "	2720 "	2676 weak.	2500 weak, wide.
2637 "	2718 "	2674 weak.	2416 about 0.5 A. U. wide.
2634 strong.	2712 strong.	2668 "	2406 about 0.7 A. U. wide.
2630 weak.	2709 "	2666 "	2395 wide.
2627 wide.	2706 weak.	2660 "	
2620 "	2704 "	2654 "	
2601 weak.	2701 "	2652 "	
2599 "	2699 "	2641 "	
2593 "	2697 "	2639 "	
2589 head of strong band.	2688 strong.		
2541 weak.			
2538 "			
2530 head of strong band.			

Alcoholic solutions of furane, thiophene, and pyrrol show no bands according to Purvis.[1] Neither do the liquids furfuraldehyde, thiophene, or pyrrol have any absorption bands.

THEORY OF DYNAMIC ISOMERISM.

Baly, Stewart, Desch, and others have recently supported the view that the absorption of light by organic compounds does not take place under ordinary conditions, but only when there is a change in the union of the atoms. In some cases this change of union takes place when a chemical compound changes into an isomeric form. Dynamic isomerism exists when there is some third substance to act as an intermediary. Many substances are isodynamic only at high temperatures or in the presence of a catalytic agent. Sometimes the solvent may promote isomeric change. The point of equilibrium is determined by the velocities of the isomeric change, and these velocities are affected by the solvent, concentration, temperature, catalytic reagent, or the presence of free alkalis or acids.

An example of the above change is the transfer of a labile hydrogen atom from an oxygen or sulphur atom to a carbon or nitrogen atom. Sometimes an OH or CN group is transferred in the same way. The atom or radical transferred assumes a neutral condition compared with its condition as a powerful negative radical in the inorganic acids.

The theory of dynamic isomerism is useful in explaining a large number of phenomena in organic chemistry, and especially those connected with light emission and absorption. Tschugaeff[1] has examined some five hundred compounds for triboluminescence (luminescence due to the crushing of the compound) and has found that 25 per cent of the organic compounds investigated showed a more or less intense flash when crushed. Most of the luminescent compounds could have existed in several isodynamic forms. Phosphorescence and fluorescence may be explained as being due to a dynamic isomerism existing between two or more forms. For instance, fluoresceïn may exist in two or more forms:

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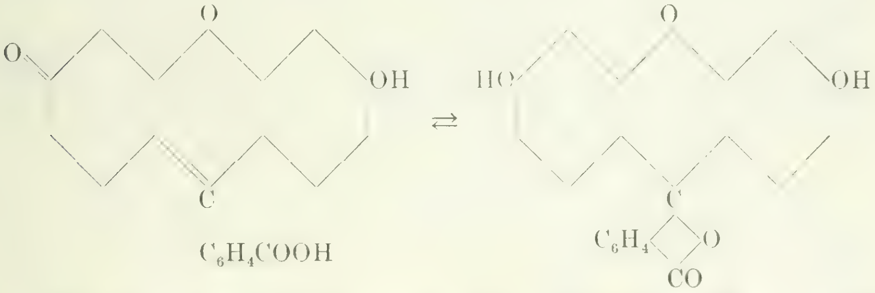
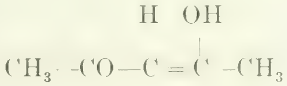
[1] Journ. Chem. Soc., 98, 1618 (1910).

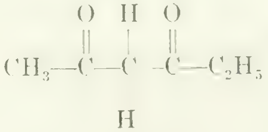


We shall now consider some recent work by Baly and Desch. They first took up acetylacetone, $CH_3—CO—CH_2—CO—CH_3$, and ethyl acetacetate, $CH_3—CO—CH_2—CO_2C_2H_5$, and their metallic derivatives. Acetylacetone and its metal derivatives were found to give similar spectra. Ethyl acetacetate was found to give only a very slight general absorption, whereas its aluminium derivative gave a spectrum almost exactly like that of acetylacetone. The work of Perkin and others has shown that free acetylacetone is enolic and ethyl acetacetate ketonic.



$$CH_3—CO—\overset{H}{C}=\overset{OH}{C}—CH_3$$

Acetylacetone (enolic).



$$CH_3—\overset{O}{\overset{\|}{C}}—\underset{H}{\overset{H}{C}}—\overset{O}{\overset{\|}{C}}—C_2H_5$$

Ethyl acetacetate (ketonic).

These results would then indicate that the metallic derivatives of ethyl acetacetate have the enolic structure, the metal taking the place of hydrogen in the OH group. But by using various compounds it was shown that neither the ketonic group, $—\underset{H}{\overset{H}{C}}—\underset{O}{C}—$, nor the enolic group, $—CH=\underset{OH}{C}—$, gives rise to a trace of banded absorption. This would also result from Hartley's work.

It would seem probable, then, that the absorption was not to be attributed to any definite molecular structure, but to a dynamic isomerism existing between the two modifications of the compound in solution. It was stated before that alkalis and acids change the velocity of the transformation from one form to the other, the final state being unaffected by the catalytic agent. This latter condition means that the direct and reverse actions are equally changed. If now intra-molecular change is the source of the absorption bands, then a catalytic agent should affect the persistence of the band. Experimental results verified these conclusions. Other compounds were tried with similar results.

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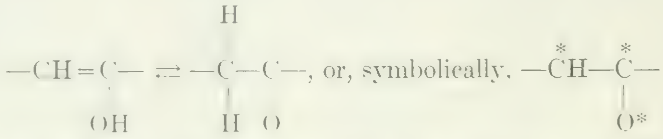
[1] Ber. d. chem. Ges., 34, 1820 (1901).

From these results it follows that there must exist, in connection with the reversible transformation of one tautomeric form into the other, a system that is synchronous with the light absorbed. This can not be a vibration of the labile atom itself, since the oscillation frequency of the absorption bands does not bear any direct relation to the mass of the labile atom, and the frequency of atomic motions is never so high as these. The absorption must be due, however, to the oscillation of linking of the keto-enol tautomers:



$$-CH=\underset{OH}{C}- \rightleftharpoons -\overset{H}{\underset{H}{C}}-\underset{O}{C}-,\ \text{or, symbolically, } -\overset{*}{C}H-\overset{*}{\underset{O^{*}}{C}}-$$

where the asterisks indicate the points where the migrations of linkages occur. From a summary of work previously done on ultra-violet absorption spectra, it was seen that most of the compounds showing absorption also were tautomeric. As was also seen, an increase in the mass of the molecule in general decreased the oscillation frequency of the absorbed light, although by only a small amount.

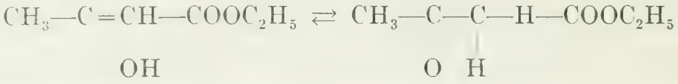
Assuming the saturnian form of atom similar to the arrangement assumed by Sir J. J. Thomson, chemical bonds would simply consist of Faraday tubes of force. By a rearrangement of Faraday tubes, it is quite probable that a vibrational disturbance would be set up. If Hewitt's explanation of the origin of fluorescence is correct, it would follow that disturbances set up by isodynamic changes are of the same frequency as light waves. The luminosity due to thermal or electric action is caused by rapid changes of stress or of the electric action to which the atoms are subjected. Here the disturbances of the electrons are due to the oscillation of linkages within the molecule. The comparatively small displacement of the absorption band by a change in the mass of the molecule is to be expected, since an increase in the mass of matter near a vibrating electron has the effect of retarding its motion, the oscillation frequency becoming less. For instance, the spectral series of Kayser for various related elements show a displacement towards the red on increasing the atomic mass. This is in general true for all emission spectra and for the absorption spectra of the rare earths and organic dyes.

The sodium and aluminium derivatives of ethyl acetacetate show the enolic and ketonic modifications in dynamical equilibrium. The sodium compound is found to be easily decomposed into sodium hydroxide and ethyl acetacetate, whereas the aluminium derivatives show dissociation and hydrolysis to only a very slight extent. The absorption spectrum is not dependent on ionization or hydrolysis. Hartley has found that the ultra-violet absorption spectra of metallic nitrates is exhibited even on very great dilution, showing a close connection between the anion and cation in such solutions. Baly and Desch conclude that the Faraday tubes may be lengthened out on dilution, and that the force necessary for the separation is furnished by the attraction of the solvent. Solvents which thus exert a strong attracting force are ionizing agents; and this attraction is exerted both on molecules and ions. We have thus hydrated molecules and ions. When the Faraday tubes are lengthened beyond a certain critical value, an interchange of ions between the molecules becomes possible. A completely dissociated solution of a salt is not one in which the ions are moving independently of one another, but one in which the length of the Faraday tubes is greater than the critical value. In tautomeric compounds the Faraday tubes connect the labile atom with the rest of the molecule, being lengthened out to such an extent as to allow these atoms to change their positions in the molecule, and there is a sort of internal ionization within the molecule. To this making and breaking of Faraday tubes may be attributed the absorption of the light.

In the tautomeric aliphatic compounds the substitution of an alkyl group for the labile atom destroys the tautomerism. This would be expected, since alkyl ions are unknown. Water and other solvents do not have sufficient attractive force to lengthen out the Faraday tubes in this case. Whether there is a banded absorption in these cases is not stated. One consequence of the theory can be tested. Since the persistence of the absorption band is a measure of the number of molecules undergoing transformation at any moment, this persistence should reach a limit for each tautomeric compound when the length of the Faraday tubes has reached their critical length, so that free interchange takes place. By the successive addition of an accelerating compound a maximum should be found. Experiment shows this to be true. Take the case of ethyl benzoylsuccinate, to which 1, 10, 20, and 100 equivalents of sodium hydroxide have been added. The limits of persistence referred to a 0.0001 normal solution of the ester are as follows:

	Free ester.	1 eq. NaOH.	10 eq. NaOH.	20 eq. NaOH.	100 eq. NaOH.
	mm.	*mm.*	*mm.*	*mm.*	*mm.*
Absorption band begins at	120.0	63.0	40	31.7	21.9
Absorption band ends at	83.2	34.7	20	15.2	10.4
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Change of dilution over which the band persists	30.7	44.9	50	52.0	52.5

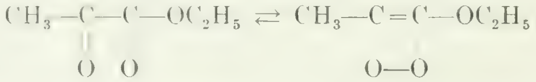
At this point it may be well to refer to the work of Stewart and Baly. Quite a number of chemical facts have been explained by the theory of steric hindrance, although this theory also fails to explain a great many things. For instance, acetic acid, CH_3COOH, is esterified with ease. The methyl, ethyl, etc., derivatives are much more difficult to esterify. This is explained as due to the larger volumes occupied by these radicals, and the consequent hindrance to the approach of the alcohol to the carboxyl radical. If, as is probable, however, the intra-molecular mean free path is large compared with the size of these radicals, this explanation in terms of steric hindrance breaks down. The theory of isodynamic change will explain all these facts and also others where the theory of steric hindrance would lead to conclusions directly contrary to the facts. According to this theory acetacetic ester exists as



$$CH_3—\underset{OH}{C}=CH—COOC_2H_5 \rightleftarrows CH_3—\underset{\overset{\|}{O}}{C}—\underset{H}{C}—H—COOC_2H_5$$

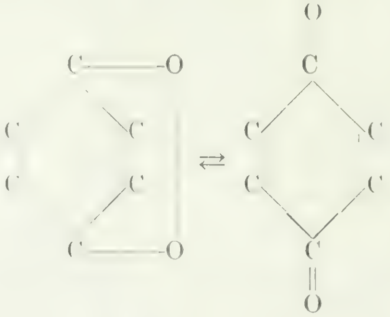
During this dynamic equilibrium there are periods during which a nascent carbonyl group exists. From analogy to the action of other nascent substances, this would occasion a very much greater reactivity.

Stewart and Baly, on further investigation, found that the absorption band in this case has a persistence which decreases proportionately to the decrease of reactivity of the ketone's carbonyl group. It has been noticed by chemists that the velocity of tautomeric change depends on the solvent. Stewart and Baly also found that the persistence of the absorption band was very different in aqueous and alcoholic solutions. In the case of pyruvic ester they show that the facts may be represented by the scheme



$$CH_3—\underset{\overset{\|}{O}}{C}—\underset{O}{C}—OC_2H_5 \rightleftarrows CH_3—\underset{O—}{C}=\underset{O}{C}—OC_2H_5$$

In tautomerism we have a wandering of the hydrogen atom, so Stewart and Baly propose to call this process isorropesis (from the Greek word *ἰσορροπεῖα*, equipoise), or an oscillation in the carbonyl grouping. By the persistence of absorption bands it is possible to measure the activity of chemical compounds. The band produced by the isorropesis is also much nearer the red than that produced by the process of enol-keto tautomerism. An example of isorropesis would be the quinone band 1/λ=2480, which would be due to the following change:



In general, then, according to the theory of Baly, Desch, Stewart, and Collie, any absorption by organic compounds is due to the conditions that occur during isomeric changes. Benzene, for example, appears in two forms, and the absorption spectrum is due to a condition of benzene while it is changing from one form to the other. This theory explains quite well the action of chromophores, since, as we have seen, every chromophore contains at least one double bond.

Theory of Stark.

Stark[1] considers that chemical valency can be explained as due to the presence of negative electrons that hold the positive parts of atoms together. In fig. 1 it is seen how this can take place, the dotted lines representing lines of electric force.

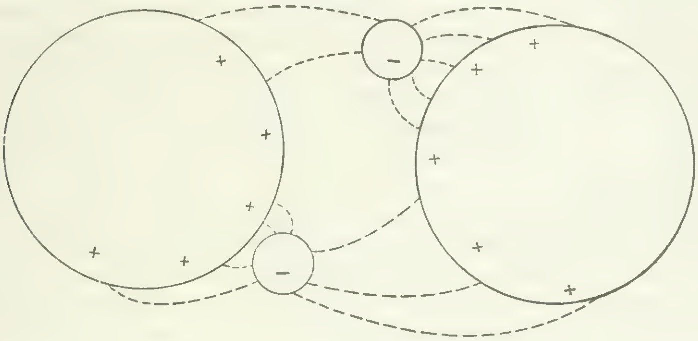


Fig. 1.

The conditions represented in fig. 1 are such that there is very little stray electric field beyond the atoms. Under such conditions the valency electrons are saturated and Stark represents this by the symbol —•. Under many conditions, however, the valency electrons are not so closely united to the atoms and are more or less unsaturated. Under certain conditions an electron may be thrown off from the atom, and Stark considers that it is under some condition such as this that selective absorption of light takes place. When the electron returns to the atom it will undergo certain accelerations along its path, and during these accelerations it will emit radiations. Stark believes that under some condition at least similar to this, the fluorescent radiation is emitted, and that the period of this radiation will depend on the amount of energy set free when an electron recombines with the positive part of the molecule. From the heat changes that occur in various chemical reactions, Stark calculates what the approximate period of these radiations should be, and in many cases obtains values which agree with the positions of known bands in the spectrum. Among these bands is the ultra-violet band of benzene. Stark's formula for benzene would be the following:

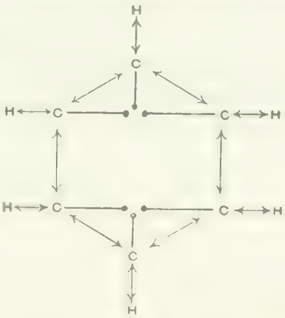


Fig. 2.

The symbol —• simply means that one electron is not as closely joined as the other three to the carbon atom. It is possible that even this unsaturated electron may have lines of force running to the other carbon atoms. In this way partial valency can easily be explained.

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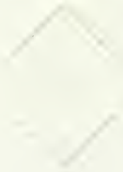
[1] Phys. Zeit., 9, 85 (1908).

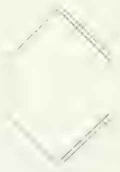
In this consideration of atoms it would be expected in general that the space containing the electric field of the electron would more or less envelop the positive nuclei of the atoms, and that the volumes of atoms would depend on their valency. This would agree very well with the assumptions of Barlow and Pope.[1] These assumptions are as follows: In any chemical body the relative volumes of the atoms are proportional to their valencies; in a crystallized body the atoms are close packed; in a compound the volumes of the spheres of atomic influences of atoms of the same valency may differ slightly. The latter variation of the sizes of the spheres of influence (interpreted here as the space filled by the electric fields of the valency electrons) may be due to the different amounts of saturation, or, as Stark calls it, the lack of the valency electrons. It would be interesting to know whether the energy relations support this view, it being expected that the greater the lack of the electrons, the less the potential energy of the compound.

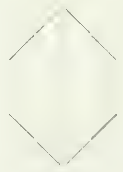
Stark and Steubing[2] have investigated the fluorescence of a large number of organic compounds. Most spectra are banded, and a band never runs in both directions. The band consists of a tail where the smaller bands are close together. From the tail the small bands may run towards the red or towards the ultra-violet, getting farther and farther apart all the time. But there are never small bands on both sides of the tail. The absorption of light by bands running "to the red" is not accompanied by fluorescence or by any photoelectric effects. The absorption of light in bands running towards the violet (benzene bands) is accompanied by a photo-electric effect, a fluorescence of the bands themselves and by a fluorescence of bands due to the connection of carbonyl, ethylene, or other chromophoric groups if these be present in the molecule. The addition of more chromophores to the compound shoves the fluorescent bands to the red.

OTHER BENZENE THEORIES.

There are some color changes of benzene compounds for which the general theory does not seem easily to account. For instance, nitronaphthalene is yellow. By introducing two nitro groups a colorless compound is obtained. In order to explain phenomena of this kind Kauffmann[3] assumes that the introduction of groups into a benzene nucleus may change the condition of the benzene ring itself. He considers that benzene may have the diagonal, the Kelulé, or the Dewar[4] formula.


I.


II.


III.

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[1] Pope: Journ. Chem. Soc., 89, 1675 (1906); 91, 1150 (1907). Swartz: Amer. Chem. Journ., 37, 638 (1907); 42, 158 (1909).

[2] Phys. Zeit., 9, 481, 661 (1908).

[3] Zeit. phys. Chem., 50, 530 (1905). Ber. d. chem. Ges., 37, 2941 (1904).

[4] Ber. d. chem. Ges., 33, 1725 (1900); 34, 682 (1901); 35, 3668 (1902). Zeit. phys. Chem., 55, 547 (1906).

In condition I benzene has an aliphatic character, as in nitrobenzoic acid, $C_6H_4(NO_2)COOH$. In this condition, having no double bonds, it does not possess strong color properties. The second condition has an aromatic character and is exemplified in the phenols. Examples of the third condition are found in aniline, *p*-phenylenediamine, naphthalene, or anthracene. Of the three conditions, the second one is the best chromophore. According to Kauffmann, benzene vapor exists in the diagonal condition, and for that reason it is not luminous when exposed to electric discharges of high frequency or to the rays from radium. Auxochromes and chromophores cause the benzene to become luminous, and for this and other reasons Kauffmann thinks that the condition of the benzene grouping has been changed.

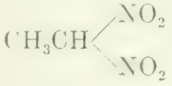
The different changes in color may be due to one or more of three conditions:

(1) There may be no intramolecular changes of constitution, but the whole change of color may be due to the change in the radicals.

(2) There may be an intramolecular rearrangement.

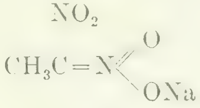
(3) There may be an association of the molecules or compounds formed with the solvent. The above classification includes color changes that are not explained by isomerism.

In many cases it is practically impossible to decide between the different possibilities. Auwers[1] and Tuck[2] give evidence to show that the sodium salt of hydroxyazobenzene owes its color simply to the introduction of the sodium. Baly and Schaefer,[3] Hantzsch,[4] Vey, Gorke,[5] and others, give some cases coming under class 2. As an example, we may take dinitroethane:



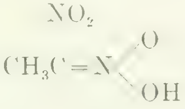
$CH_3CH\begin{matrix}\diagup NO_2\\ \diagdown NO_2\end{matrix}$

Pseudo acid, colorless.



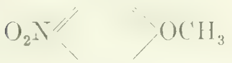
$\begin{matrix}NO_2\\ CH_3C=N\begin{matrix}\diagup O\\ \diagdown ONa\end{matrix}\end{matrix}$

Sodium salt, yellow.

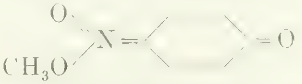


$\begin{matrix}NO_2\\ CH_3C=N\begin{matrix}\diagup O\\ \diagdown OH\end{matrix}\end{matrix}$

Acid, yellow.



Nitrophenol ether, faintly yellow.
Benzene derivative.



Chromonitrophenol ether, deep red.
Quinone derivative.

A very full discussion of the "Umlagerung" theory is given by Ley.[6] A short discussion is also given of the theory of indicators, of polymerization, and of metallic derivatives of organic compounds, especially of cases where the metal is supposed to be present in the inner part of the molecular complex.

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[1] Lieb. Ann., **360,** 11 (1908).

[2] Journ. Chem. Soc., **91,** 454 (1907).

[3] *Ibid.,* **93,** 1806 (1908).

[4] Hantzsch: Ber. d. chem. Ges., **32,** 575 (1899). Hantzsch and Veit: *Ibid.,* **33,** 626 (1900). Ley and Hantzsch: *Ibid.,* **39,** 3149 (1906).

[5] Hantzsch and Gorke: *Ibid.,* **39,** 1073 (1906).

[6] Jahrb. d. Rad. u. Elek., **6,** 341, 381 (1909).

CHAPTER II.

EXPERIMENTAL METHODS AND APPARATUS.

In this work the mapping of the spectra was done in the same way and by the same methods as already described in Publication No. 130 of the Carnegie Institution of Washington, pages 19-22. The general arrangement of apparatus is given in fig. 4.

New difficulties that required special treatment quite frequently presented themselves in the work. As an example, one might take that of mapping the absorption spectrum of solutions of samarium, dysprosium, and gadolinium salts, very kindly lent us by Professor Urbain. In order to bring out as many bands as possible, the absorption cell was made wedge-shaped, the apex of the wedge being about 2 mm. wide and about 15 mm. long. In this way a much greater cell depth could be obtained with the same amount of solution than with the Uhler cell. Another difficulty consisted in getting the strip of the photographic film uniformly exposed. The appearances of bubbles, of precipitates, etc., during the heating of the solutions are further examples. In some cases these difficulties could be overcome. For instance, if the Uhler cell was moved back and forth in the path of the beam of light, bubbles and precipitates only decreased the amount of light passing through the solution and did not cause an uneven exposure on the strip.

Part of the work consisted in extending the Beer's law tests to very dilute solutions. Some work was done on uranyl solutions, using a trough with plane parallel ends. Other cells consisted of glass tubes with quartz lenses at the ends. One of these was 500 cm. long. With cells of this kind it is impossible to obtain a uniform exposure, unless the cell is moved back and forth in the path of the beam of light.

Salt solutions that have bands in the violet and ultra-violet were exposed for much longer intervals of time than those which have bands only in the visible part of the spectrum. In making an exposure of this kind (the uranyl salts are typical examples) the length of exposure to the shorter wave-lengths would be from 5 to 10 times longer than to the longer wave-lengths. First, an exposure would be made to the whole spectrum of the Nernst glower; then a screen would be placed in front of the plate, cutting out all light of wave-length greater than about λ 4500 or λ 4800. A long exposure would then be made to the short wave-length spectrum of the glower; and lastly, a short exposure would be made directly to the spark.

For high-temperature work on acid solutions the fused silica cell was used, while for room temperatures this cell and the Uhler cell were used for such solutions.

Part of this investigation consisted in extending the work on absorption spectra to high temperatures, by means of closed cells. Two cells, one 1.0 cm. and the other 10 cm. in length, were used. Fig. 3 represents a longitudinal section of the longer cell. Since both cells were exactly alike in all respects except in length and in the size of the side tube, only the longer cell will be described here. The main part of the cell (T) was made of tool steel and was heavily copper plated and gold plated on all the inner surfaces.

The side tube was very tightly fitted into the main part of the horizontal tube. The open part of the tube was 1.0 cm. in diameter. The windows of the cell (U, U) were 2.5 cm. in diameter and were either of quartz or glass. One of the troubles with this form of cell is the formation of precipitates on the inside surfaces of the windows. Every time a precipitate is formed, the windows have to be taken out and cleaned. On being put back there is always great danger of the quartz or glass ends being broken. During the work a number of ends were broken in this way.

Quartz ends are much tougher and less easily broken than glass ends. They are, however, quite expensive and in most of the work the solutions were not transparent in the ultra-violet. For this work glass ends were used. Some of these were cut out of ordinary plate glass and others were made from "uviole" glass, which is tougher and much more transparent in the ultra-violet than the ordinary plate glass. For cutting the ends a steel tube was fastened to the axle of an ordinary fan motor. The steel tube was 2.5 cm. in diameter and the motor was placed so that the tube was vertical, the free end of the steel tube being at the bottom. An old glass end was then cemented to a piece of plate glass with hot sealing wax and served as a guide for the steel tube. The plate glass was then held against the end of the steel tube and the motor started. Wet carborundum was fed constantly against the grinding steel tube. Plates nearly 1.0 cm. thick could be cut in this way in 20 or 30 minutes.

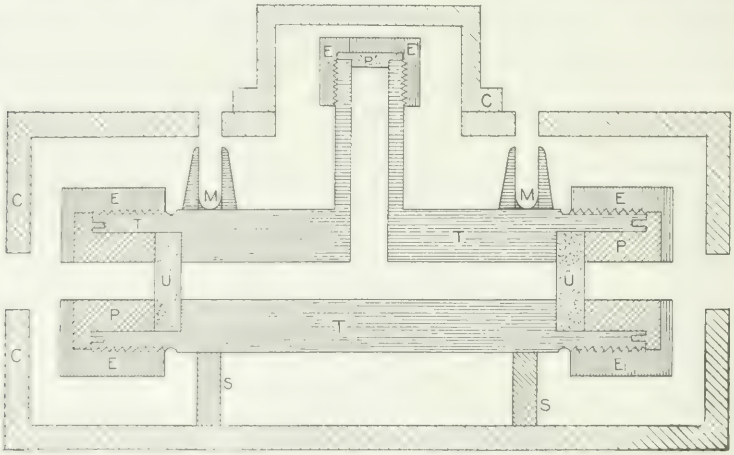

Fig. 3.

The quartz windows rested on gold washers, and these rested directly against the gold-plated shoulders of the tube T. PPP are plungers. Two of these at the ends of the main tube have guide pins that prevent the plungers from turning. Between the plungers and the windows were placed washers. Various kinds of washers of hard leather, lead, zinc, etc., were used. The leather washers, however, seemed to be the most satisfactory. Steel caps, *EEE* serve to tighten the plungers. *MM* are receptacles for thermometers for measuring the temperature. *C* is an iron air-bath and protects the cell from rapid changes in temperature.

In heating a cell of this kind it was found that the rise in temperature should be very gradual. Very great difficulty was encountered in getting the ends to hold liquid tight. The screw ends were tightened gradually for several days and for several heatings. On one occasion, when the tube was filled with one of the higher alcohols, a very effective closing was made. It is possible that dried films of oils (like linseed oil) might be of use as washers.

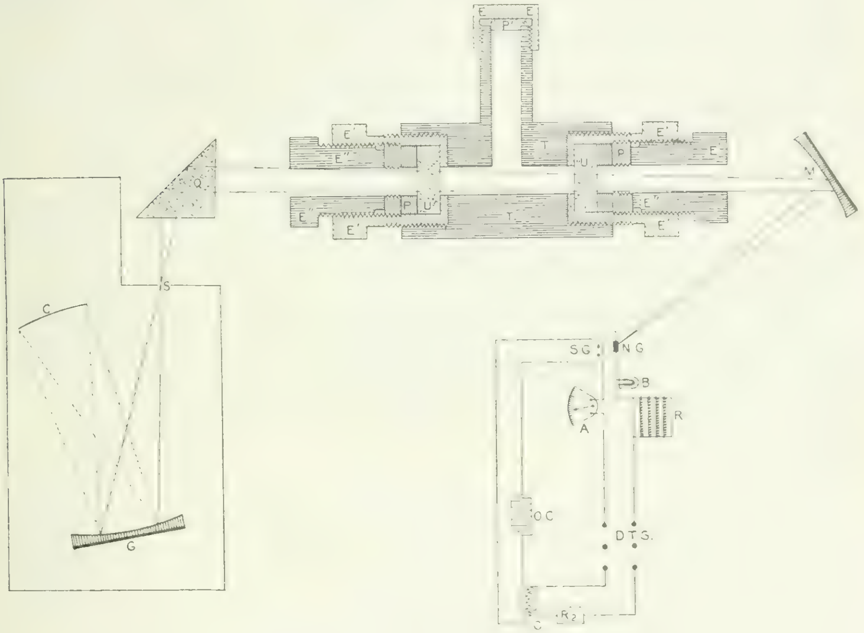

FIG. 4.

In beginning the work no serious trouble from the formation of precipitates was anticipated. This interference was encountered and a new form of cell is being made which it is hoped will overcome some of the imperfections of the form above described. In this form (fig. 4) the quartz ends are fastened in the ends *E′* in the same way as in fig. 3. Instead of the plunger *P* having guide pins it has guide grooves. Part of the plunger has screw threads, by means of which it can be taken out. The whole cap can be removed from the tube *T* by unscrewing *E′*, during which the quartz end is untouched. When the ends are removed the quartz window can easily be cleaned. Gold washers are required here between *T* and *E′* and between *E′* and *U*.

The remaining parts of fig. 4 represent a diagrammatic arrangement of the apparatus. Only the cell is drawn to scale. The cell was kept in a horizontal position so that all bubbles that form would rise in the side tube. As the spectroscope (containing the grating *G*, photographic plate holder *C*, and slit *S*) was kept in a vertical position, a 45° quartz prism was used to change the horizontal beam of light into a vertical beam, the beam being totally reflected by the hypothenuse surface of *Q*. The source of light *N.G.* (Nernst glower) or *S.G.* (spark gap) was focused by the concave speculum mirror *M* on the slit *S*. A similar arrangement was used with the fused silica cell. *D.T.S.* represents a double throw switch, by means of which either the Nernst glower or the spark gap may be thrown in circuit. *B* is a ballast. *R* is a variable resistance, by means of which the current (read by the ammeter *A*) in the Nernst glower may be kept constant.

O.C. is an oil condenser. Some trouble was given by the condensers, especially when a large spark gap (2 or more centimeters) was used for several hours. Paraffin condensers often become heated so that the paraffin melts. A condenser was made of transformer oil. Unfortunately, the box part was made of wood and it is very difficult to prevent the leaking of the oil from such a box, especially when it becomes heated. *I.C.* is an X-ray induction coil and R_2 is a resistance in the primary circuit of this coil.

Some preliminary tests were made with the cells at high pressure. The Cailletet pump belonging to the University was used for this purpose, the cell represented in fig. 3 being made so as to fit on this pump. It was not at all difficult to obtain pressures of 200 atmospheres with water and alcohol solutions. Spectrograms were made of the absorption spectra of neodymium solutions under pressures as high as 275 atmospheres. No effect of pressure was detected. The work at high pressures is easier than at high temperatures, on account of the fact that there is no expansion of the cell due to heating.

CHAPTER III.

MAPPING THE ABSORPTION SPECTRA OF VARIOUS SALTS IN SOLUTION.

An accurate knowledge of the absorbing power of solutions is the first requisite in understanding the nature of absorption, and, accordingly, the mapping of the spectrum is the first thing to be done. This has been accomplished for a large number of solutions, but there are quite a few salts that have thus far been omitted, and it is the purpose of this chapter to give the results with some of these solutions. This has been made possible largely through the kindness of Professor Urbain, who has loaned us the oxides of samarium, dysprosium, and gadolinium. Dr. Guy has converted these oxides into the various salts such as the chloride, nitrate, etc., and has dissolved these in various solvents. The other salts whose absorption spectra have been investigated have been obtained, for the most part, from Kahlbaum. The numbers of plates described in this chapter run from 1 to 34 inclusive.

Jones and Anderson have shown that the absorption bands of a given salt in any solvent were characteristic of that solvent. For this reason the photographing of the absorption spectra of a given salt in different solvents will be considered as the mapping of characteristic spectra. On the other hand, when a salt is gradually changed to another salt by the addition of an acid to the solution, or by the addition of a foreign salt, the absorption bands show *gradual changes.* This has been interpreted as being due to changes in the molecular aggregates of the salts, and to the formation of intermediate compounds. These changes are considered as being of a chemical nature, and will, therefore, be taken up in the chapter dealing with the spectrophotography of chemical reactions; and the facts there described will be regarded as furnishing strong evidence for the existence of molecular clustering in liquids, and also for the theory that the absorption and emission centers of spectrum bands consist of more or less complex atomic or molecular aggregates, probably in a process of ionization. The full development of this view appears in the summary.

The experimental methods are essentially those described in Publication 130 of the Carnegie Institution of Washington, and in the chapter on experimental methods in this monograph. Nothing more need be said here, except that it would probably be desirable in some cases to place the negative film of an absorption spectrum just below the photographic film that is being exposed. Then, by lengthening the time of exposure very greatly, it should be possible to get a spectrogram containing a great many bands.

THE ABSORPTION OF CERTAIN CYANIDES AND CHROMATES.

The early workers on absorption spectra supposed that if two salts, dissolved in the same solvent, had absorption bands that were close together, the wave-lengths of the bands would be modified by the salts being together in the solution. Experiments of this kind have been made without much success. According to the theory of aggregates, however, it would not be expected that any very marked effect would result, unless the two salts formed parts of the same aggregate; the term aggregate being used in the broader sense here to include also molecules of the solvent. Accordingly, the list of colored chemical compounds was searched for salts that contained colored anions and colored cations. An effort was also made to obtain solvents and salts that had bands in the same part of the spectrum. So far no good examples were found where the same spectral aggregates contained different absorbing centers that possess bands in the same region of the spectrum. It seems quite possible, however, that aggregates of this kind among organic compounds could be found, or that in the infra-red region many examples of this kind will be found. The region of the infra-red is especially inviting for work of this kind, inasmuch as nearly all groups possess bands, and the absorbers seem to be of molecular dimensions; whereas in the visible portion of the spectrum it seems probable that, in most cases at least, the constitution of the spectral aggregate only influences the period of vibrators that seem to be of the nature of electrons.

It has been shown that the presence of calcium or aluminium chloride has a considerable influence upon the wave-lengths of the uranyl chloride bands. This has been explained[1] as being due to the presence of chlorine, rather than to the direct presence of the calcium or aluminium atoms. It is possible to obtain aqueous solutions of calcium ferricyanide or of aluminium and calcium chromate. If the change of wave-lengths of the uranyl bands was not due to calcium and aluminium, then the absorption of the potassium, aluminium, and calcium ferricyanides and chromates should be the same. These salts were studied to test whether or not this was the case.

The dissociation[2] of the ferricyanides, ferrocyanides, and chromates is an interesting one, and the study of the absorption spectra of solutions of these salts, especially in the infra-red, will probably throw much light upon this subject, but in this work time did not permit us to take up this problem.

Calcium Ferrocyanide and Calcium Ferricyanide.

The absorption spectrum of calcium ferricyanide is given in plate 2, *A*, and of calcium ferrocyanide in plate 2, *B*. The concentrations are given in the chapter on the description of plates. Starting with strip 1 of *A*, the edge of the absorption band is at about λ 4700; the concentration (*c*) being 0.031 normal and the depth of cell (*d*) 24 mm. (hereafter the product *cd* will be given without definition, *c* being expressed in terms of normal and *d* in millimeters), the value of *cd* being 0.74. In the case of potassium ferricyanide[3] for a value of *cd* of 0.69 the edge of the absorption band comes at about λ 4690, considering the limit of absorption as at λ 4710 and the distance between this limit and the place where the absorption is 50 per cent as being 20 Angström units. It is thus seen that the absorption of calcium ferricyanide is approximately the same as that of potassium ferricyanide. The conclusion follows that calcium shows no bathochromous effect in this instance.

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[1] Phys. Zeit., 11, 668 (1910).

[2] Publication 130, Carnegie Institution of Washington, 28 and 29.

[3] *Ibid.*, 29.

In strip 1, *B*, plate 2, *cd* is 6 and the middle of the edge of absorption is at about λ 4150, the edge of the band being about 300 Ångström units wide. The edge of the absorption is very wide and diffuse, resembling the absorption of potassium ferrocyanide. No direct comparison of the absorption in the two cases can be made, as the value of *cd* is much larger in the case of the calcium salt.

The Chromate and Bichromate of Lithium.

The absorption spectrum of an aqueous solution of lithium chromate is given in *A*, plate 1, and of lithium bichromate in *B*, plate 1. In the case of lithium chromate a change in *cd* of 0.75 to 6.0 produces an increase in width of the absorption of over 200 Ångström units; the edge of the band being at about λ 4850 for $cd = 0.75$. This is approximately the position of the edge of the absorption band of potassium chromate for a corresponding value of *cd*. For lithium bichromate, the edge of the absorption for strip 1, $cd = 0.75$ is about λ 5350. The values of *cd* here are much larger, and the absorption is, therefore, much greater than in the case of potassium bichromate previously investigated.

Aluminium and Calcium Chromates.

The absorption spectrum of an aqueous solution of aluminium chromate is given in *A*, plate 3. The depths of cell are 3, 24, 24, and 24 mm. Starting with the lowest strip the solution used in strip 1 was the same as in strip 2.

In *B*, plate 3, is given the absorption of an aqueous solution of calcium chromate, the depths of cell being 24 mm. and the concentrations 0.025, 0.033, 0.046, 0.066, 0.1, 0.15, and 0.2 normal. For a value of *cd* of 0.6 the edge of the absorption is at about λ 4670. For corresponding values of *cd* it seems, therefore, that the absorption of calcium chromate is less than the absorption of lithium or potassium chromate, and that the presence of calcium does not increase the width of the absorption bands.

Potassium Nickel Chromate and Copper Bichromate.

The absorption of these two salts is an example of the absorption of salts in which both the anion and the cation are colored. *A*, plate 4, represents the absorption of an aqueous solution of copper bichromate, the depths of cell being 3, 24, 24, 24, 24, 24, and 24 mm. and the concentrations 0.044, 0.044, 0.08, 0.117, 0.175, 0.26, and 0.35 normal. *B* gives the absorption of an aqueous solution of potassium nickel chromate. *A* is seen to show the edge of the red copper band. For a value of *cd* of 0.13, the edge of the absorption in the blue is about λ 4900, which is seen to be about the same as that for potassium bichromate. The absorption of salts having both ions colored does not seem to be at all different from what one would expect if the absorption was additive. Of course, these experiments are very largely qualitative, and it is expected that a rigorous examination along quantitative lines will be made with the radiomicrometer. For photographic methods the above salts are not at all well suited, since the limits of absorption and transmission are very large and ill defined.

The Absorption of Solutions of Certain Erbium Salts.

On account of the slight solubility of the erbium chloride in the higher alcohols and other organic solvents, very few solutions could be made of sufficient concentration to show the erbium absorption bands. Several of these will be taken up under the effect of change in temperature on absorption spectra.

Hofmann and Kirmreuther[1] have examined the absorption spectra of certain salts of erbium, using the reflection method, and find a very marked similarity between the spectra of all of the salts investigated, although these may be as different as the chloride and sulphide of erbium. For this reason they conclude that the erbium bands are due to locked electrons and not to saturated valency electrons.

THE ABSORPTION OF SOLUTIONS OF CERTAIN NEODYMIUM SALTS.

Previous work has shown us that neodymium and uranous salts show characteristic solvent spectra better than any other colored salts. On account of the sharpness of the neodymium bands, neodymium salts have been made the object of especial study for the existence of solvent spectra. In many cases it is known how the neodymium bands break up in a magnetic field, and in general it is probably true that the absorption of salts of this element has been studied more than that of any of the others. It seems, therefore, probable that ultimately some knowledge of the forces within the solvate may be learned, when it is found how the various neodymium bands are broken up for the different kinds of solvates. In the following pages considerable emphasis will be laid upon the finer structure of the neodymium bands for solutions in the various solvents. A large field of investigation is open for the study of the difference in the structure of these bands in solids and especially in crystals. Only a few examples of the latter kind will be described here.

In the description of the groups of neodymium absorption bands, the following nomenclature will be used. This is done for the reason that each one of these groups of bands possesses a characteristic structure for the various solvents, and very often for different salts in the same solvent. While the groups of bands do not change greatly in relative intensities, the finer bands in each group show most extraordinary changes of this kind. The α group includes bands in the region λ 3400 to λ 3600; the β group the bands at about λ 4300; the γ group from λ 4600 to λ 4800; the δ group from λ 5000 to λ 5400; the ϵ group in the region λ 5800 and the ζ group at λ 6300. In the general discussion of results these groups will be compared under various conditions of temperature, solvent, acid, etc.

In the measurements of the wave-lengths of the neodymium bands, the standard spark lines were photographed only in the ultra-violet, so that the measurements of the long wave-length bands here given are not claimed to be very accurate and are made largely for comparison. On the other hand, the difference in wave-length of bands in the same group is much more accurate.

In designating the groups of bands of the neodymium spectra, previous workers started with the red end of the spectrum. This, however, is an unnatural method of procedure when a grating is used, since the spectrograms are all printed with the short wave-lengths on the left side, with the wave-lengths increasing linearly as we pass towards the right. Moreover, it is very doubtful if the ultra-violet absorption spectra of neodymium can be investigated much farther in this region, so that this is the natural end of the spectrum from which to begin naming the groups of bands. On the other hand, it is very probable that there are many more neodymium bands in the infra-red, and if these occur in groups, these groups can then be named in their proper order. The reason that the uranyl series of absorption bands was named in the opposite direction was on account of the fact that the strongest of these bands are at the red end of the series, while the weak bands are in the ultra-violet, the weaker ones of the series in many cases still remaining to be photographed.

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[1] Zeit. phys. Chem., **71**, 312 (1910).

NEODYMIUM CHLORIDE IN WATER.

Some of the weak and fine bands of neodymium and uranium are extremely difficult to obtain clearly on a photographic plate, and it has sometimes seemed to us that the presence of absorption bands of some wave-lengths might be due to some absorber that was not always present in the solution. For instance, the presence or absence of foreign nuclei might be a determining factor in the constitution of the aggregates. It might also be possible that aggregates in solution are quite stable as far as their inner constitution is concerned, so that an aqueous solution of neodymium chloride, for instance, might show different absorption bands depending upon what the species of neodymium chloride aggregates was before the salt was dissolved. It might be possible to detect phenomena of this kind. It would also be very interesting to find whether there is any relation between the kinds of spectral aggregates of a salt in solution, and the ionic and nucleating centers produced by spraying or bubbling the solution. Nuclei of various salts have been investigated in this manner by Broglie and others. The spray from solutions of the same salt in two or more solvents could be taken up. Samarium and uranous salts could be studied in the same manner.

Plate 60, *B*, in the original film shows bands at λλ 4000, 4180, 4271, 4280, 4295, 4330, 4650, 4695, 4805, 5330, etc. So far as we remember, this is the first plate of an aqueous solution on which the very narrow and faint band at λ 4280 has clearly appeared. The band λ 4805 is also a very weak one. In the first strip of the original film, the band λ 4271 possessed very sharp edges and was about 8 Ångström units in width. The band λ 4280 was very weak and was not more than 1.5 or 2 Ångström units wide. The band λ 4295, on the other hand, was about 8 Ångström units wide and very weak. λ 4650 is very weak and is seldom seen.

An attempt will be made to compare as much in detail as possible the bands at λ 4280, λ 5200, and λ 5800 for the various solvents, since it is these bands that give evidences of the existence of solvates and the various aggregates.

NEODYMIUM CHLORIDE AS A METHYL ALCOHOLATE.

A solution of neodymium chloride in methyl alcohol, that had been allowed to stand over the summer, was found to contain a gelatinous precipitate. The absorption spectrum was found to show the neodymium bands quite sharply, these bands having a somewhat different appearance from those in an ordinary methyl alcohol solution.

A sharp band appears at λ 4270, a weaker band about 8 Ångström units wide at λ 4295; a wide weak band at λ 3440; the triplets at λλ 4700, 4760, and 4830; a very weak band at λ 5100; a wide hazy band at λ 5140; two strong, sharp bands at λ 5220 and λ 5235; a wide and weak band at λ 5260, and bands more or less blurred together at λλ 5704, 5780, 5815, and 5860. It will be noticed that the bands at λ4270 and λ4295 are relatively stronger than usual. The appearance of these two bands suggests that the precipitate is largely the hydrate of neodymium chloride, the band λ4270 being a water band, and the band λ4295 being an alcohol band.

Neodymium Chloride in Propyl Alcohol.

The only spectrogram of the absorption spectra of neodymium chloride in propyl alcohol that is reproduced is that of *A*, plate 7.

The α group is composed of the following bands: λ 3445, a rather sharp band about 4 Ångström units in width; λ 3460, about 10 Ångström units in width; λ 3490 of about the same intensity and width as λ 3460; λ 3510 very weak; λ 3525 about 4 Ångström units wide and quite strong; λ 3540 quite strong and narrow, this band almost running into the more diffuse band at λ 3560; a very weak band appears at about λ 3580. The β group is quite characteristic of the solvent, consisting of a very weak band at about λ 4270, a band at λ 4285 about 10 Ångström units wide, and a much wider and weak band at about λ 4330; a wide and weak band appears at λ 4450. The γ group consists of a very weak and diffuse band at λ 4600, and other bands at λ 4700, λ4770, and λ4830. The δ group consists of two wide and diffuse bands at λ 5130 and λ 5180, the latter being very weak; and finer bands at λ 5220, λ 5230, λ 5250, λ 5290 and a very weak band at λ 5330. The ϵ group consists of the four bands λ 5740, λ 5780, λ 5810, and λ 5850, all being of about the same width, the latter two being considerably the stronger. There are other bands in the red region, but only λ 6880 is at all strong.

Neodymium Chloride in Isopropyl Alcohol.

A, plate 6, gives the absorption spectrum of neodymium chloride in isopropyl alcohol. The finer structure of the different groups of bands is quite different from that of the propyl alcohol spectrum.

The α group of this alcohol is very simple, showing only three hazy bands, at λ 3460, λ 3510, and λ 3535, the middle band being much the weaker. Only a single band of the β group shows, λ 4265. Other bands appear at λ 4420, λ4600 very diffuse, λ4690 and λ4730.

The δ group consists of λ5100 and λ5320. These bands are quite wide and diffuse. On account of the plate not being properly developed the bands do not show as much detail as they probably would under more favorable conditions. Even this plate shows the finer bands slightly.

The ϵ group consists of a broad diffuse band at λ 5720 and two much stronger bands at λ 5780 and λ 5810.

Neodymium Chloride in Butyl Alcohol.

The absorption spectrum of neodymium chloride in butyl alcohol is given in plate 5, *A*. Starting with the ultra-violet, we have λ3450 very sharp and narrow; λ 3460 weak; λ 3492 somewhat diffuse; λ 3535 very sharp and narrow; λ 3545, λ 3560 very diffuse. The bands λλ 4265, 4285, and 4300 are weak and of approximately the same intensity, the band λ 4265 being slightly narrower than the other two. These bands differ not only in relative intensity from the water bands but also in wave-length, band λ 4265 being of shorter wave-length and the band λ 4300 of greater wave-length than the water bands.

The other bands are quite diffuse and appear at λλ 5085 (narrow), 5095 (narrow and very weak), 5130, 5200, 5215, 5240, 5270, 5300, 5710, 5750, 5780, 5820, 5860, 5900, and 5930.

This plate is described in detail in the chapter at the end of the monograph. It may be noticed that for the solution of greatest length, the absorption in the ultra-violet is very strong, extending to λ 4100. This is probably due to the propyl alcohol. It is certainly not due to the absorption of the neodymium chloride itself.

Neodymium Chloride in Isobutyl Alcohol.

A, plate 8, represents the absorption spectrum of neodymium chloride in isobutyl alcohol. It will be seen from the wave-lengths given below that there are quite marked differences between the absorption in this alcohol and that in butyl alcohol. The band λ 3455 is about 10 Ångström units wide, and is quite weak in the above photograph, λ 3485 is of about the same width and is much stronger, λ 3515 is very weak, λλ 3545 and 3570 are of about the same intensity and each 10 Ångström units wide. There seems to be a very weak band at about λ 4300. Wide and very diffuse bands appear at λλ 4550, 5120, 5220, 5250, 5720, 5780, 5800, 5850, and 5890. The four bands last mentioned are of about equal intensity.

The general characteristics of the absorption spectrum of neodymium chloride in isobutyl alcohol are the weakness and diffuseness of the bands in general, their different relative intensities compared with butyl alcohol bands, and their slightly greater wave-lengths. The butyl alcohol bands are very much finer and sharper than the isobutyl alcohol bands. In general, it seems that the shorter the wave-lengths of the solvent bands the finer and sharper are those bands.

Another spectrogram taken of a solution containing a much longer layer contains the following bands: The β group λ 4270, a very weak and narrow band; λ 4290, a weak band about 6 Ångström units wide; λ 4310, the strongest band in the group, being a little stronger than λ 4290; λ 4330 weak and quite diffuse, completing the bands of this group; a very wide (50 Ångström units) diffuse band appears at λ 4450; the γ group consists of bands about 20 Ångström units wide at λ 4700, λ 4730, λ 4780, λ 4830, and λ 4880, this band being very weak; the δ bands at λ 5150 and λ 5260 are about 80 Ångström units in width and consist of smaller bands that appear practically fused together; some of the finer bands being at λ 5215, λ 5230, λ 5250, and λ 5300; the ε group composed of the following bands: λ 5740 rather weak, λ 5810 strong, λ 5850 strong, λ 5890, λ 5920, λ 5950 very weak, λ 5995 very weak, and λ 6020 very weak.

The ultra-violet absorption of isobutyl alcohol is very considerable and prevents the α bands from being shown very plainly. The smaller bands are also more numerous, although weaker than in most other solvent spectra.

Neodymium Chloride in Ether.

Neodymium chloride is only very slightly soluble, if soluble at all, in ordinary ether. By adding a small amount of a concentrated solution of neodymium chloride in methyl alcohol to ether, a solution of about 0.01 normal was obtained. At about 10° C. this solution is transparent and its absorption was photographed. Heated to about 35° C. a white precipitate was formed, making the solution quite opaque. When cooled again the solution became transparent. A solution of this kind might serve to give us a better knowledge of the constitution of aggregates. Suppose it could be shown, spectroscopically, that the neodymium chloride aggregates existed in the ether as the methyl alcoholate, and that when the cloud was formed the ether solution was completely freed from any neodymium salt. The number of cloud particles could easily be counted with an ultra-violet microscope and the size of the neodymium aggregates thus approximately determined. A study of the Brownian movements and the growth of such a cloud would also be interesting. It might be possible in some case to obtain a transparent solution of colored solvates in a solvent having the same index of refraction and density as the solvate, but not miscible with it, and by heating such a solution the liquid of the solution and the solvate might mix at higher temperatures and the resultant salt aggregate, if insoluble, would then be precipitated.

NEODYMIUM NITRATE IN PROPYL ALCOHOL.

B, plate 7, represents the absorption spectrum of neodymium nitrate in propyl alcohol. The absorption bands of this spectrum are quite diffuse and present a sort of washed-out appearance.

The α group consists of three bands, the inner band being the wider and weaker. These bands are nearly 20 Ångström units wide and are located at λ 3455, λ 3500, and λ 3585. The β group consists of but a single band about 12 Ångström units in width at about λ 4268. The γ and other bands in that region are very broad and weak. The δ group is resolvable into the single bands λ 5100 and λ 5220. For the greater concentrations, however, two bands can be distinguished near the center of λ 5220, being at about λ 5220 and λ 5235. The ε group consists of the hazy bands λ 5700, λ 5750, λ 5780, and λ 5810.

NEODYMIUM NITRATE IN ISOPROPYL ALCOHOL.

The absorption spectrum of neodymium nitrate in isopropyl alcohol resembles quite closely the general diffuseness of the propyl alcohol spectrum previously described.

The α group consists of three hazy bands at λ 3460, λ 3505, and λ 3535. Each of these bands is about 15 Ångström units in width. The β band is weak, being located at λ 4270. Bands appear at λ 4430, λ 4690 and λ 4730. The δ group consists of a band at λ 5100 and one at λ 5230. The latter consists of a wide, diffuse, short wave-length component, and two finer bands that resemble very closely the corresponding propyl alcohol bands. The ε group consists of a weak hazy band at λ 5720, and two stronger bands at λ 5790 and λ 5810.

NEODYMIUM NITRATE IN BUTYL ALCOHOL.

The absorption spectrum of neodymium nitrate in butyl alcohol is given in the first two strips of *A*, plate 9. The general characteristics of the bands is their general diffuseness.

The α group consists of three diffuse bands, the outer bands being much the strongest at λλ 3450, 3500, and 3540. The β group consists of a band at about λ 4265, and a very weak band at about λ 4280. Weak and diffuse bands appear at λ 4420, λ 4690, λ 4730, and λ 4820. The other bands are at λ 5090, λ 5220, λ 5710, λ 5800, and λ 5930.

The absorption spectrum of neodymium nitrate in butyl alcohol resembles very closely the spectrum in isopropyl alcohol, but is quite different from the spectrum in isobutyl alcohol.

Neodymium Nitrate in Isobutyl Alcohol.

The absorption spectrum of neodymium nitrate in isobutyl alcohol is similar to that of the chloride in the same alcohol. The bands in some cases are not so wide, but they are all quite weak when they first appear in the spectrum. The ultra-violet absorption was so great that in the plate taken the α group does not appear at all. At λ 4285 appears a weak double band about 15 Ångström units wide. These bands are so close to one another that it is difficult to be certain that they are separate bands. There are also very weak bands at λ 4305 and λ 4325. The β group of the chloride in isobutyl alcohol is very different in its structure from that of the β group of the nitrate. A very weak band appears at λ 4450 and λ 4600, which is about 80 Ångström units wide. The γ group consists of weak bands, each about 20 Ångström units in width at λλ 4715, 4750, 4770, and 4850. The δ group consists of the wide and very hazy band at λ 5120, two comparatively weak bands at λ 5215 and λ 5230, and three strong bands that practically merge into each other at λ 5245, λ 5255, and λ 5275. The ε group forms a single wide band extending from λ 5730 to λ 5900. Very hazy and weak bands appear at λ 6000, λ 6050, and about λ 6800.

The composition of the various groups of the nitrate isobutyl bands is quite different from the chloride bands. This is a general phenomenon, the nitrate bands, in general, being quite different from the chloride and bromide bands in the same solvent.

Neodymium Nitrate in Acetone.

The absorption spectrum of neodymium nitrate in acetone also consists of wide, diffuse, and weak bands. The ultra-violet absorption is large.

The following bands appear: λ 4285 very weak, λ 5130, λ 5250, λ 5750 and λ 5840.

Neodymium Nitrate in Ethyl Ester.

The absorption spectrum of neodymium nitrate in ethyl ester is given in *A* and *B*, plate 12, and *B*, plate 10. The absorption bands of this spectrum are in general quite diffuse. The α group consists of three hazy bands, the middle one being much the weakest at λλ 3455, 3500, and 3540. The β group consists of a single band about 15 or 20 Ångström units wide at about λ 4270. The bands at λ 4440 and λ 4600 are very broad and weak. The γ group is quite different from the γ group of other solvents, in that the bands are not even approximately of the same intensity or at equal distances from each other, being at about λ 4710, λ 4730, and λ 4830. The δ group consisted of λ 5120, λ 5210, λ 5240, and λ 5260. The ε group consists of λλ 5700, 5750, 5780, and 5810. These bands are very diffuse, about 20 Ångström units wide, and the latter two are much the stronger. A band also appears at λ 5980.

The absorption spectrum of neodymium nitrate in methyl ester is identical with that in ethyl ester.

Neodymium Acetate in Acetone.

The absorption spectrum of neodymium chloride in acetone has bands that are much more diffuse than the corresponding water bands. Similarly, the acetone bands of the acetate are more diffuse than the water bands, and both spectra are more diffuse than the chloride spectra.

The α group of the acetate in acetone apparently consists of but a single band, quite weak, at λ 4270 and about 15 Ångström units wide. The region λ 4300 to λ 5100 is practically continuous, the bands appearing there being so weak and diffuse that they can hardly be detected. The δ group consists of a wide diffuse band at λ 5110 and finer bands at λ 5200 (weak), λ 5235, λ 5250, and λ 5260; the latter three practically blending into one. The ε group extended from λ 5720 to λ 5860, this absorption showing a weak band at λ 5730, about 30 Ångström units in width. From the above description it will be noticed that there is a strong ultra-violet absorption (reaching to λ 3900), and that the neodymium bands themselves are very wide and diffuse.

Neodymium Acetate in Formamide.

A, plate 13, represents the absorption spectrum of neodymium acetate in a formamide solution. The absorption bands of this solution are quite wide and diffuse, but not as much so as the bands of the acetate in acetone. The ultra-violet absorption is so strong as to prevent the appearance of the α group. The β group consists of a band at λ 4285, which is about 10 Ångström units wide. The bands λλ 4440, 4690, 4750, 5110, and 5230 are wide, diffuse, and with the exception of the latter, are all very weak. The ε group consists of four diffuse bands that run into each other at λλ 5710, 5740, 5790, and 5830.

Summary of Neodymium Spectra.

α *Group in Water.*—Neodymium chloride in water gives λ 3390 a very weak band, λ 3465 narrow and strong, λ 3505, λ 3540 narrow and strong, and λ 3560. The anhydrous chloride gives a rather strong and narrow band at λ 3500, a weaker band at λ 3537, narrow and intense bands at λ 3570 and λ 3595, and a rather hazy band at λ 3612.

α *Group in Methyl and Ethyl Alcohols.*—The chloride shows the bands λλ 3475, 3505, and 3560. These bands are much hazier than the water bands. The latter one is by far the most intense. The nitrate in methyl alcohol has two bands, λ 3465 and λ 3545.

α *Group in Acetone.*—The nitrate has rather faint and wide bands at λ 3475 and λ 3555.

α *Group in Glycerol.*—The chloride gives a weak band at λ 3520, and strong and sharp bands at λ 3475 and λ 3550.

β *Group in Water.*—Neodymium chloride in water gives a very sharp band at λ 4271, and a very narrow and weak band at λ 4290. The anhydrous salt gives narrow and intense bands at λ 4308 and λ 4313, a wider band at λ 4333 and a narrow band at λ 4357. Neodymium nitrate in water has a band at about λ 4280, which is more hazy than the λ 4271 chloride band, and which breaks up into a band at λ 4271 and a sort of shading on the red side of this band at about λ 4280.

β *Group in Methyl and Ethyl Alcohols.*—A band appears at λ 4290 about 10 Ångstrom units wide. This is wider and fainter than the water band at λ 4271. λ 4325 is still fainter than λ 4290. The nitrate in methyl alcohol gives a band at λ 4280, which is not very intense, and which is about 10 Ångström units wide.

β Group in Acetone.—The nitrate has the band λ 4280 quite weak and about 15 Ångström units wide.

β Group in Glycerol.—This group in glycerol consists of a sharp and very persistent band at λ 4288, and two very fine bands of the same intensity at λ 4270 and λ 4305.

γ Group in Water.—For the chloride there is a band at about λ 4610 with hazy edges; λ 4645 a very weak band; a band at λ 4685 with its red edge the more sharply defined; a rather sharp band at λ 4755 and one at λ 4820, which is narrow and quite intense. The anhydrous chloride gives faint and hazy bands at λ 4640 and λ 4680, narrow and intense bands at λ 4717, λ 4725, λ 4735, λ 4785, λ 4815, and λ 4855. The nitrate shows bands at λ 4737, λ 4755, λ 4772.

γ Group in Methyl and Ethyl Alcohols.—There are bands at λ 4700, λ 4780, and λ 4825. These bands are of about the same intensity, λ 4780 being somewhat the narrower. λ 4700 and λ 4825 have faint companions to the violet. The nitrate shows three faint bands at λλ 4690, 4735, and 4825.

γ Group in Glycerol.—Glycerol bands of the chloride appear at λλ 4620, 4710, 4730, 4760, 4790, and 4840.

δ Group in Water (Green).—The bands in this group form a rather complicated series. The chloride has a deep narrow band at λ 5090, a wide hazy band at λ 5125, a pair of very intense, narrow bands at λ 5205 and λ 5222, a narrow band at λ 5255, and a faint, hazy band at λ 5315. The anhydrous chloride gives a weak band at λ 5088, λ 5117, a narrow, intense band at λ 5147, λ 5174, λ 5183, λ 5216, λ 5254, λ 5267, λ 5282, etc. The nitrate band at λ 5090 is much wider and hazier than the corresponding chloride band, whereas the nitrate band at λ 5125 seems narrower. There is a narrow band at λ 5205, a much more intense one at λ 5225, and another narrow band at λ 5235. There seems to be a tendency for the chloride and nitrate spectra to become much more alike as the dilution is increased.

δ Group in Methyl and Ethyl Alcohols.—These bands are λ 5125 hazy and moderately intense; λ 5180 hazy and fainter; λ 5220 intense and narrow; λ 5245 intense with faint companion on the red; λ 5290 narrow and a faint band at λ 5315. The nitrate has two rather intense bands at λ 5225 and λ 5240.

δ Group in Acetone.—The nitrate has a hazy, but rather intense band at λ 5110, λ 5215, and λ 5255.

δ Group in Glycerol.—The chloride gives bands at λλ 5120 wide and hazy; 5170 narrow; 5190 narrow; 5230, 5240, 5250, and 5270 weak.

ϵ Group in Water (Yellow).—For the chloride, this group consists of a narrow and quite strong band at λ 5725, a strong doublet at λ 5745 and λ 5765, a band at λ 5795 very similar to the one at λ 5725, although more hazy. The anhydrous chloride has bands at λ 5768, λ 5782, a narrow and intense band at λ 5807, λ 5829, a narrow band at λ 5858, etc.

ϵ Group in Methyl and Ethyl Alcohols.—This group consists of λ 5725 moderately intense with hazy edges; λ 5765 narrower; λ 5800 strong; λ 5835 very intense; λ 5860 hazy; λ 5895 faint; λ 5925 faint. The nitrate shows a band at λ 5720, probably double, a band from λ 5755 to λ 5845 and at λ 5760, λ 5835, and a very intense band at λ 5790.

ϵ *Group in Glycerol.*—The chloride gives the following bands: λλ 5740 hazy, 5790, 5805, 5820, and 5850.

Although the absorption spectra of the dry neodymium salts are very different from one another, those of the aqueous solutions, especially when dilute, are very much the same for the different salts. For concentrated solutions the chloride is very similar to that of the bromide, but these are quite different from the nitrate.

The absorption spectra of neodymium chloride in methyl alcohol and in ethyl alcohol are practically the same, and differ considerably from that of the nitrate. The absorption bands of the nitrate in ethyl alcohol are, in general, more diffuse than in methyl alcohol.

The chloride is but slightly soluble in acetone. The absorption spectrum of the nitrate in acetone is especially characterized by the weak and hazy appearance of the bands.

The absorption spectrum of neodymium chloride in glycerol is more like that of the water spectrum, in that the bands are often very sharp and narrow.

The absorption spectra of the chloride and nitrate in isobutyl alcohol are quite different. The structure and distribution of the intensity of the absorption in each group is entirely different. The center of gravity of the absorption of each group is considerably farther to the red in the case of the chloride, but the composition of the groups is so different for the two salts that no relationship can be seen between them when the individual bands are compared. These solutions would afford a very good example for the spectrophotography of chemical actions in isobutyl alcohol at low temperatures.

The above summary is made simply to give a few of the conclusions reached in previous publications from this laboratory on absorption spectra, and could be extended almost indefinitely. As the subject has not been studied exhaustively, it is only given as typical of what should be done later. In the present chapter the water, methyl and ethyl alcohols and glycerol solutions were not taken up. For a further treatment the reader should refer to the chapters that are to follow. On account of lack of time, the work on this subject must be regarded as just begun. The following is the purpose of the investigation. In the case of the uranyl bands it was found possible in many instances to trace the bands by gradual changes from one salt to another. By this means it was hoped to study chemical reactions in various solvents, to find if a chemical reaction had the same effect on the uranyl bands under different conditions. For a similar reason the neodymium spectrum has been broken up into groups of bands, and it was proposed to study these minutely as conditions were changed. The purpose here is to give a description of as many characteristic groups as possible, and to correlate the groups that are alike. It might be assumed, when the groups were constituted of the same bands with the same relative intensity, sharpness, etc., that the physical and chemical environment of the absorbing centers was the same, etc. Much more work of the above kind remains to be done, especially with the rare earths already described, erbium, holmium, etc. The absorption of the dry salts, the phosphorescent spectra, and the absorption spectra at low temperatures should be obtained. This, naturally, brings us to the subject as it is presented in the two chapters that follow.

THE ABSORPTION SPECTRUM OF SOLUTIONS OF CERTAIN SALTS OF URANIUM.

For a full discussion of the absorption spectrum of a large number of uranium solutions the reader should consult Publication No. 130 of the Carnegie Institution of Washington. In the following pages only a few solutions are discussed, these being for the most part solutions of the uranyl salts in some of the organic solvents. This was taken up because corresponding neodymium solutions were being investigated, and it was thought to be of some interest to study a few uranyl solutions in the same way. In the description of the bands of uranium solutions it must be remembered that the terms wide, fine, sharp, narrow, broad, etc., are relative to other uranyl or uranous bands and not to neodymium or samarium bands. A sharp uranyl band would, therefore, be a very wide and hazy neodymium band.

Uranyl Chloride in Propyl Alcohol.

The absorption spectrum of uranyl chloride in propyl alcohol is given in *B*, plate 18. The absorption bands of the propyl alcohol solution are quite strong and appear at the following positions: λλ 3980, 4100, 4230, about 4400 (this band is apparently double), 4580, 4750, and 4910. The upper strip shows quite well the difference in intensity of the *a* and *b* bands. In this strip the *b* band is very broad and strong, running from λ 4690 to about λ 4820. On the other hand, the *a* band is quite weak, and is not more than about 40 Ångström units in width.

Uranyl Chloride in Isopropyl Alcohol.

A, plate 14, gives the absorption spectrum of uranyl chloride in isopropyl alcohol. The blue-violet band is seen to be quite prominent, its middle coming at about λ 4350, about 100 Ångström units farther towards the red than for the aqueous solutions. The uranyl bands are very weak and diffuse, being much more so than for the propyl alcohol solution. The *a* band does not appear on the spectrogram. The following bands show: λ 4100, λ 4250, λ 4360 (these two bands practically merge into one another), λ 4560, and λ 4750.

Uranyl Chloride in Butyl Alcohol.

The absorption spectrum of uranyl chloride in butyl alcohol is given in the three upper strips of *A*, plate 15. It will be seen that the uranyl bands are very wide and diffuse. The following bands can be distinguished from the general absorption: λλ 3850, 3960, 4100, 4240, 4390, 4560, 4750, 4970. The bands are all very diffuse, the last band being about 150 Ångström units in width.

Uranyl Chloride in Isobutyl Alcohol.

The absorption spectrum of uranyl chloride in isobutyl alcohol is given in *B*, plate 19. The spectrogram gives the following uranyl bands: λλ 4400, 4560, 4720, and 4900.

Uranyl Chloride in Ether.

The following uranyl bands have been photographed for a solution of uranyl chloride in ether: λλ 4040, 4160, 4300, 4444, and 4630. The solubility of uranyl chloride in dry ether is very small.

Uranyl Chloride in Methyl Ester.

The uranyl bands show quite strongly in the methyl ester solution of the chloride. The bands are as follows: λ 4030(*g*), λ 4160(*f*), λ 4280(*e*), λ 4440(*d*) (this band may be double and thus really represent *de* instead of simply *d* as given above), λ 4620(*c*), λ 4790(*b*), and λ 4920(*a*). The *a* band is very weak, compared with the *b* band. Beyond the *a* band towards the red, there is a very weak band which is so weak that it is very difficult to distinguish it from the absorption of the blue-violet band itself.

Uranyl Chloride in Ethyl Ester.

B, plate 14, represents the absorption spectrum of a solution of uranyl chloride in ethyl ester. The absorption bands are very strong and are quite sharp. The wave-lengths and general appearance of the bands are practically the same as that of the methyl ester solution previously described.

Uranyl Chloride in Formamide.

B, plate 15, represents the absorption of a solution of uranyl chloride in formamide. The uranyl bands appear quite strong, especially the long wave-length bands. The three bands in the second strip appear of about equal intensity at λ 4450, λ 4650, and λ 4840. The latter band is probably the *b* band. The *a* band does not appear at all on the spectrogram.

Uranyl Nitrate in Propyl Alcohol.

B, plate 21, represents the absorption spectrum of uranyl nitrate in propyl alcohol. The absorption bands are quite strong and sharp, and appear as follows: λλ 3640, 3750, 3850, 3970, 4080, 4190, 4320, 4470, 4640, and 4820. The latter band is probably the *a* band, as it is very much narrower than the band at λ 4640.

Uranyl Nitrate in Acetone.

The photograph of the absorption spectrum of uranyl nitrate in acetone showed only three bands. These bands were quite narrow, but were not as sharp as the chloride bands. They are at λ 4510, λ 4660, and λ 4830.

Uranyl Nitrate in Methyl Ester.

The absorption spectra of uranyl nitrate in methyl ester is given in *A*, plate 15. The bands are rather weak, appearing at λλ 3900, 4000, 4110, 4220, 4340, and 4480.

Uranous Chloride in Propyl Alcohol.

The absorption spectrum of uranous chloride in propyl alcohol is given in *A*, plate 18. The absorption bands are all quite strong, especially the uranyl bands. The uranyl bands shown most prominently are those at λ 4590 and λ 4750, each about 80 Ångström units wide, and a very wide band at λ 4950 about 150 Ångström units wide. Two fine bands appear at about λ 5190 and λ 5210. These bands are about 10 Ångström units in width. A band at λ 5500 is about 120 Ångström units in width. A group of three narrow bands appears at about λ 5720, λ 5750, and λ 5770. The middle band is the strongest one of the group, and is about 15 Ångström units wide. Absorption maxima appear at about λ 6100, λ 6270, and λ 6520. This whole region is one of more or less general absorption, due to the above very wide bands. The band at λ 6720 is very similar to the uranyl bands at λ 4590 and λ 4750. The general appearance of these uranous bands in the red is very much like that of the aqueous uranous bands.

URANOUS CHLORIDE IN ISOBUTYL ALCOHOL.

A, plate 20, represents the absorption spectrum of uranous chloride in isobutyl alcohol. The uranous bands of this absorption spectrum appear quite sharp, especially when they are broad, as is the case in the upper strips of this spectrogram. The first strip shows a double band at about λ 4300. These bands practically merge, especially in the other strips, the shorter wave-length band being much more intense. Quite a sharp band appears at λ 4950, with a broad region of absorption on the violet side. With a larger amount of salt this absorption is greatly increased, resulting in a very great widening of the band on the violet side, while the red side widens but little. A band appears at λ 5480, a weak band at λ 6300, a strong band from λ 6400 to λ 6600, and a strong band at λ 6720. The spectrogram shows the total absence of the uranyl bands, and very slight absorption in the region of the ultra-violet. The upper strip shows the wide uranous bands very sharply indeed.

URANOUS CHLORIDE IN METHYL ESTER.

B, plate 24, represents the absorption spectrum of uranous chloride in methyl ester. From the absorption spectrum it is apparent that the uranyl salt has been largely reduced, since the uranyl bands do not show at all. Uranous bands appear at λ 4300 (about 120 Ångström units in width). There is a region of strong absorption extending from about λ 4700 to λ 5100, with the strongest absorption in the longer wave-length portion of this region; resulting in a much greater widening of the band towards the violet as the amount of salt in the beam of light is increased. There is a band at λ 5500 about 150 Ångström units wide and the red bands appear. The red bands are both rather wide, the stronger and narrower one being at λ 6730. In strip 3 the absorption runs from λ 6400 to about λ 6760. As the absorption increases this red absorption region widens very unsymmetrically towards the region of shorter wave-lengths. This solution, like most other clear uranous solutions, shows very little general absorption in certain regions of the spectrum. Even the general absorption in the ultra-violet is not so very great. When a large amount of the solution is placed in the beam of light, considerable light still passes through, and the edges of the absorption bands appear quite sharp.

THE ABSORPTION CENTERS OF URANIUM SPECTRA.

Important results will probably be obtained by a study of uranyl and uranous compounds at low temperatures. It might be possible to obtain aggregates of sufficient size to be seen by the ultra-violet microscope, or to be observed in a manner somewhat similar to that of the scintillation method of observing the α rays on a phosphorescent screen. The uranyl aggregates could be illuminated by flashes of ultra-violet light and by proper sector arrangements the aggregates could be viewed in the intervals between the illumination. These aggregates should then appear as centers of the green uranyl phosphorescence. Neodymium compounds in phosphorogens could possibly be treated in the same manner. These salts should also be studied when under bombardment by β rays, if they do not show any effect by α rays. Recent studies of phosphorescent screens subjected to α-ray bombardment has led to the belief that these substances are composed of aggregates.

THE ABSORPTION SPECTRUM OF GADOLINIUM.

Very little has been done on the absorption spectrum of gadolinium. A dilute nitrate solution in a 10 mm. layer showed several weak bands at λ 3500 to λ 3390, with a maximum at λ 3470. A weak band appeared at λ 3300 to λ 2890 and continuous absorption commenced at about λ 2200. According to Soret there is a band from λ 2800 to λ 2450.

Gadolinium Chloride in Water.

B, plate 28, shows the absorption of a solution of gadolinium chloride, 1.407 normal; the depths of cell starting from the lowest strip being 2, 10, 15, 22, 22, and 100 mm. The spectrogram shows that there is quite a strong, general absorption in the ultra-violet, amounting to several hundred Ångström units in the case of the 2 mm. length of layer, transmission beginning at about λ 2700. For the 100 mm. length of layer this absorption extends to about λ 3700, the edge of the transmission being very broad.

The plate shows, besides this general absorption, two very sharp bands at λ 2925 and λ 2980. These appear clearly for the 10 mm. layer. For the 100 mm. layer a weak band, about 25 Ångström units in width, appears at λ 3910. A very weak band appears at λ 3970. This band is so weak that it can hardly be seen in the original film.

Gadolinium Chloride in Ethyl Alcohol.

Plate 28, *A*, gives the absorption of a 0.8 normal solution of gadolinium chloride in ethyl alcohol; the depths of cell, starting from the lowest strip, being 2, 4, 9, 18, 27, and 27 mm.

One of the most pronounced characteristics of the absorption of this alcoholic solution is the enormous absorption in the ultra-violet, compared with the aqueous solution. The edge of this absorption is very diffuse. It extends to about λ 3000 for the 2 mm. solution, and to about λ 4400 for the 27 mm. solution.

The only characteristic part of the absorption spectrum is a very diffuse band at λ 4360. This band is gradually included in the region of general absorption, as the depth of cell is increased.

It will be noticed that the absorption spectra of the alcohol and aqueous solutions are very different indeed.

THE ABSORPTION SPECTRUM OF DYSPROSIUM.

Very little work has been published on the absorption spectrum of dysprosium. Lecoq de Boisbaudran[1] has described the following bands arranged according to the intensity of the bands: *Dyα*, λ = 4515; *Dyβ*, λ = 4750; *Dyγ*, λ = 7565; *Dyδ*, λ = 4275.

Urbain[2] has observed only λ 4740 and a weak band at λ 4530 to λ 4500.

[1] Compt. Rend., 102, 1005 (1886). [2] Ann. Chim. Phys., 19, 244 (1900).

Dysprosium Chloride in Water.

The absorption spectrum of aqueous solutions of dysprosium chloride is given in *B*, plate 29, and *A*, plate 30. The absorption in the ultra-violet is very small for aqueous solutions of dysprosium chloride, even when the depth of cell is as great as 21 mm., and the concentration is 1.86 normal, as it is for the last strip of *A*, plate 30.

Strip 2, *B*, plate 29, represents the absorption of a 6 mm. layer of 1.86 normal concentration. As this strip shows many of the bands, it will be described in detail. The general appearance of the bands is much the same, although they vary greatly in intensity. The edges are quite sharp, although none of the bands are as sharp and clear as the neodymium water band, λ 4271.

The first band observed in the ultra-violet is λ 3130. As will be seen from the spectrograms the bands in the ultra-violet are by far the strongest in the spectrum. λ 3130 is one of the strongest of these ultra-violet bands, and is about 40 Ångström units wide. The next band at λ 3260 is about 20 Ångström units wide and is quite weak. It is very similar and of the same order of intensity as the bands at λλ 3470, 3670, 3690, 3800, 3850, 4170, 4340, 4400, and 4430. Of these bands, the latter two are the strongest. The band λ 3390 is the strongest band in the whole spectrum. It possesses sharp edges and is over 50 Ångström units in width, while the strong band λ 3535 has only a width of 30 Ångström units. The band λ 3760 is also quite strong and has a width of about 25 Ångström units. Other bands appear faintly at λλ 4650, 5300, and 6350, but these are so weak that their positions can hardly be measured. The band at λ 3970 is very broad and weak, and shows best in the fifth strip.

In the last strip of 100 mm. depth, quite a number of new bands appear. The ultra-violet absorption has become so strong that the whole region to λ 4050 is absorbed. The band at λ 4160 is apparently double, being much more intense on the violet side. The bands at λ 4190 and λ 4220 are much weaker, the former almost merging into λ 4160. Absorption bands extend from λ 4250 to λ 4300, λ 4450 to λ 4580, λ 4680 to λ 4820. Very weak bands appear at λλ 4840, 4890, 4930, 4960, 5425, 5460, 5490, 5520, 6460, 6570, and 6600. The band λ 5380 is quite strong and almost merges into the other bands in this region. The band λ 6440 is also quite strong. λ 6440 and λ 6460 are very diffuse and almost form a single band.

Dysprosium Chloride in Methyl Alcohol.

The absorption spectrum of a solution of dysprosium chloride in methyl alcohol is given in *A*, plate 29. The absorption is greater for the alcohol solution, especially the general ultra-violet absorption. Otherwise the relative intensity, number, wave-length, and general appearance of the absorption bands are exactly the same as the bands of the aqueous solution.

Dysprosium Chloride in Ethyl Alcohol.

With the exception of the very much greater ultra-violet absorption, the spectra of dysprosium chloride in water, methyl alcohol, and ethyl alcohol (*B*, plate 31) are very much the same; the ethyl alcohol band at λ 5400 being wider and of greater wave-length than the water and methyl alcohol bands at λ 5380.

The fact that this one band should appear of a different wave-length in ethyl alcohol, as compared with water, while the other dysprosium bands appear to be the same for both solvents, might be taken to indicate that this band was not due to dysprosium. A difference of this kind might lead to a possible method of ascertaining the presence of the salts of two different elements in solution. In the case of neodymium salts it was found, in general, that if one solvent had one characteristic band, all the solvent bands were more or less characteristic. On the other hand, it must be remembered that in the case of the uranyl bands the differences for different solvents were usually much greater for the longer wave-length bands. So, in the above case of dysprosium chloride in ethyl alcohol, we may assume that the band λ 5380 may not be due to dysprosium. It may be possible that the difference in the action of acids on the bands of the spectra of a given salt, or the difference of the spectra as obtained with the same salt in different solvents, may be useful in separating the different elements.

Dysprosium Acetate in Water.

The absorption spectrum of dysprosium acetate (0.4 normal) in water is given in *A*, plate 31. The depths of cell were 4, 16, 25 and 34 mm. The spectrum is very similar to that of the aqueous solution of the chloride. The bands are, however, somewhat more diffuse. The wave-lengths of the bands, while comparatively weak, appear to be the same for the chloride and the acetate. The acetate bands widen more to the red, so that when the bands are quite wide, the acetate bands appear to be relatively shifted towards the red. The addition of concentrated nitric acid produces little effect on the wave-length, or the appearance of the dysprosium acetate bands in water.

THE ABSORPTION SPECTRUM OF SAMARIUM.

The absorption spectrum of samarium has been studied much more extensively than that of gadolinium and dysprosium. On the following page is a table giving the wave-lengths of some of the bands as determined by various observers.

In general appearance the absorption spectra of samarium salts are very similar to those of the dysprosium salts, the strong bands of the spectrum being located in approximately the same violet and ultra-violet part of the spectrum. The general appearance of the individual bands is very similar to that of the dysprosium bands, the samarium bands being, however, somewhat narrower and having sharper edges.

Samarium Chloride in Water.

The absorption spectrum of samarium chloride in water is shown in *A*, plate 32. The concentration is 1.31 normal and the depths of cell, starting from the lowest strip, are 2, 6, 12, 16, 20, and 100 mm.

From the spectrogram it is seen that for the aqueous solution the ultra-violet absorption is very small indeed. A weak and apparently quite wide band appears at about λ 3050. For the 6 mm. depth of cell, second strip, bands appear at λλ 3200, 3320, 3510, 3630, 3910, etc. The other bands are quite weak and will be given for the 20 mm. layer. Of the above bands, the λ 3910 is by far the strongest of all the samarium bands. For the 20 mm. layer the following bands appear: λ 3420 (diffuse, about 20 Ångström units wide), λ 3470 to λ 3540, λ 3550 very weak, λ 3570 very weak, λ 3600 to λ 3660, λ 3720 very weak and wide, λ 3770 weak, λ 3800 (about 20 Ångström units wide), λ 3860 to λ 3945, λ 3970, λ 4050, λ 4070, λ 4320 very wide and weak, λ 4540 (about 40 Ångström units wide); λ 4640 to λ 4750 is a region consisting of two diffuse bands that practically run together, λ 4800 weak, λ 5110 weak. Other bands appear in the region of longer wave-lengths, but they are very weak.

A 100-mm. strip showed complete absorption of wave-lengths shorter than λ 4130. Bands appeared from λ 4210 to λ 4370; a band about 30 Ångström units wide at λ 4420; a band from λ 4470 to λ 4840, λ 4890 to λ 4950, λ 4200, λ 4230 (these two bands are of about the same intensity, rather diffuse and about 20 Ångström units wide), λ 5500, λ 5525; these bands are very similar to the preceding pair, being, however, considerably more intense.

Lecoq de Boisbandran.[1]	Soret.	Thalen.[2]	Krüss and Nilson.	Bettendorf.	Forsling.[3]	Böhm.[4]	Demarçây.	Formanek.[5]
5590	5590	5590–5560	5587	5590–5582	5600	....	5590	5588
....	....	....	....	....	....	....	5290	5282
5010–5000	5000	5015–4970	5004	5039–4995	5001	....	4980	5211
4890	4890	....	4891	....	....	....	....	5005
4860–4740	4800	4860–4720	4830–4750	4885–4736	4804–4783	4800	....	4892
....	....	....	....	....	4761–4727	....	4760	4880
4640–4630	4635	4660–4600	4633	4690–4619	4632	4625	4630	4750
....	....	....	....	....	....	....	4530	4634
....	....	4450–4370	....	....	4443–4383	....	4430	4530
4170	4190–4150	4185–4150	4174	4220–4151	4174	4165	4170	4436
....	....	....	....		4157	....	....	4175
....	4080–4060	4090	4090		4083	....	....	....
....	....				4077	....	4070	....
....	....				4035–4030	....	4020	4090
4007.5	....				4016–4007	....	....	
	....				3942–3932	....	....	
	....				3906	....	3900	
	3760–3720				3752–3742	3750–3730	3750	
	....				3738–3732	....	....	
	3640–3600				3630–3615	3640–3600	3620	

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[1] Spectres Lumineux, Paris bei Gauthier-Villars (1874).

[2] Journ. de Phys., 2, 446 (1883).

[3] Bih. K. Svensk.Vet.-Ak. Handl., 28, II. Nr. 1 (1902).

[4] Zeit. angew. Chemie., 15, 1282 (1902).

[5] Die qualitative Spectralanalyse anorganischer Körper, Berlin bei Mückenberger (1900).

Samarium Nitrate in Water.

The absorption spectrum of samarium nitrate in water is given in *A*, plate 33. The absorption bands have almost the same characteristics, relative intensity, wave-lengths, etc., that water-bands of samarium chloride have.

Samarium Chloride in Methyl and Ethyl Alcohols.

The absorption spectrum of samarium chloride in methyl alcohol, *B*, plate 32, is so similar to the absorption of this salt in ethyl alcohol, *A*, plate 34, that only the former will be described in detail. It will be seen from the spectrograms that the general absorption in the ultra-violet and violet in the case of the ethyl alcohol solution is very much greater than in the case of the methyl alcohol solution.

B, plate 32, represents the absorption of a normal solution of samarium chloride in methyl alcohol, the depths of all being 2, 5, 9, 18, 27, and 27 mm. The last spark spectrum was taken with the solution removed simply for the purpose of making wave-length measurements. The first strip shows the following bands: λ 3200, λ 3330, λ 3500, λ 3540, λ 3640, λ 3910, λ 3925, and some weaker bands farther towards the red. The third strip shows the following bands: λ 3200 quite weak; λ 3330, λ 3350, λ 3430, and λ 3450 very weak and diffuse, appearing almost as a single band; λ 3500, λ 3540, λ 3570, λ 3640; λ 3910, the strongest band in the spectrum, is about 35 Ångström units wide, λ 3950 about 10 Ångström units wide, λ 3970 about 6 Ångström units wide, λ 4060 and λ 4100 are each about 30 Ångström units wide and quite weak. Other bands are easy to see and will be described in the last strip. In this strip the ultra-violet absorption is complete to λ 3350. In addition to the bands mentioned above there were bands at λλ 4290 weak, 4310 weak, 4350 weak, 4410 weak, 4520, 4545, 4570; this triple group is perfectly symmetrical, the middle band being much the strongest; 4650, 4705, and 4760 are each about 40 Ångström units wide, are diffuse and weak with the middle band having the greatest intensity; 4810 is about 10 Ångström units in width, 4920 quite weak and diffuse, and 5200 is very weak. No other bands in the longer wave-length region are visible in addition to those described.

Samarium Chloride in Water and Ethyl Alcohol.

The absorption spectra of samarium chloride in mixtures of water and ethyl alcohol are given in *B*, plate 33, and *B*, plate 34. The change from the alcohol to the water spectrum can easily be seen in the shift of the bands of strip 1 compared with strip 2 in *B*, plate 34. The very great persistency of the water bands is shown, since in this case (strip 2) only about 5 per cent of water is present. The band λ 3970 seems to be a characteristic water band. In strip 1, *B*, plate 33, this band does not appear, but in strip 2 it can be clearly seen and in the succeeding strips it becomes stronger. It seems, therefore, that the samarium bands behave in the same way as the neodymium bands, although there is no single band that shows the effect as clearly as the neodymium λ 4271 water band, and the corresponding λ 4290 alcohol band. Since the water bands are so persistent it would be very interesting to carry this work to temperatures almost as low as the freezing-point of alcohol. In general, a lowering of temperature has increased the persistency of the water bands.

CHAPTER IV.

SPECTROPHOTOGRAPHY OF CHEMICAL REACTIONS.

INTRODUCTION.

Prior to these investigations, very little work had been done on the effects produced on the absorption spectrum of a salt in solution when acids and various other reagents that produce chemical reactions were added. Indeed, much of our knowledge of what is in solution is obtained indirectly rather than by a direct knowledge of the composition of compounds while in solution. Considerable work on the effect of the introduction of certain radicals, groups, etc., on the absorption spectra of organic compounds has been done, and a fairly complete survey of this work is given in the first chapter. Especial efforts have been made to discuss, as completely as possible, our knowledge of the absorbing and emitting centers of light and heat.

It is true that a few observers had noticed that in some cases different salts had bands of different wave-lengths, when dissolved in the same solvent. A typical example of this kind is given in the following table. Then again, observers had noted that the bands of one salt of a metal were finer and sharper than the bands of another salt (for example, neodymium chloride as compared with the nitrate in water), but, as far as we know, no effort has been made to study what changes in the bands resulted as one salt of a metal was changed into another salt.

The following table gives the absorption bands of some double acetates of uranyl according to Morton and Bolton:[2]

NH_4..................	4620	4455	4310	4200	4075
Ba..................	4625	4465	4330	4200	4075
Co..................	4625	4465	4335	4200	4080
K..................	4625	4460	4320	4200	4070
Li..................	4620	4455	4320	4205	4080
Mg..................	4627	4480	4337	4215	4085
Na..................	4620	4453	4310	4185	4055
Rb..................	4625	4465	4315	4202	4080
Sr..................	4627	4480	4335	4205	4075
Tl..................	4640	4480	4320	4205	4085
Zn..................	4655	4490	4340	4325	4100

For the following double sulphates they give:

Ammonium uranyl sulphate.....	4935	4800	4620	4450	4330	4240
Ammonium diuranyl sulphate....	4875	4720	4575	4480	4330	4210
Magnesium uranyl sulphate......	....	4790	4540	4370	4230	4100
Potassium uranyl sulphate......	....	4790	4540	4370	4230	4100
Rubidium uranyl sulphate.......	4885	4805	4645	4475	4325	4205
Thallium uranyl sulphate........	4905	4630	4480	4295	..	
Sodium uranyl sulphate........	4875	4775	4580	4440	4335	4180

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[1] Publication 130, Carnegie Institution of Washington.

[2] Chem. News, 28, 47, 113, 161, 233, 244, 257, 268 (1873).

One of the purposes of the present research is to study one group of bands throughout a long series of reactions. The first group of bands to be studied in this way was the uranyl bands. Although not completely followed, and not identified with certainty in every case, yet for aqueous solutions, at least, it has been possible to designate these bands as *a*, *b*, *c*, *d* . . . . and to follow each band as the salt is changed from acetate to nitrate, from nitrate to chloride, from chloride to sulphate, etc. It is found in all these changes that the individual uranyl bands undergo a *gradual shifting of their position in the spectrum.* Various chemical changes have been accompanied by characteristic changes in the absorption spectrum; *e.g.*, a narrowing of the bands, a shifting of the bands to the violet, etc. It is natural to try to correlate as many of these characteristics as possible, but as yet not enough work has been done to furnish many generalizations. It may be said, qualitatively, that in many instances a shifting of the bands towards the violet is often accompanied by a narrowing and sharpening of the edges of the bands. This is a general characteristic also of the temperature effect, since a lowering of the temperature of an absorbing compound is nearly always accompanied by a narrowing of the absorption bands and a slight shifting towards the violet.

Again, it is natural to inquire whether the same chemical reaction produces the same changes in the absorption spectra when this reaction takes place in different solvents. Unfortunately there are not many examples of this kind that can be tested. In general, the absorption bands of different salts in the same solvent are practically the same, so that a chemical reaction can not be photographed spectroscopically. It was for this reason that a considerable number of absorption spectra have been mapped. A number of solvents showing a difference in the absorption spectra of different salts are not suited very well for this kind of work. Some very good examples, however, have been found, and these will soon be studied. Acetone was found to give a greater difference between the absorption spectra of uranyl nitrate and the other uranyl salts than water; and as the uranyl acetone bands are very sharp and these solutions can be studied at very low temperatures, this solvent offers exceptional advantages for making a comparison between the same chemical reactions in the two solvents.

The closely related problem as to whether apparently similar chemical reactions for different salts in the same solvent are really similar has already been answered in some cases in the negative. We have seen that the chemical reaction that takes place when uranyl chloride is changed to uranyl nitrate has resulted in a narrowing and sharpening of the uranyl bands, and a gradual shifting of these bands towards the violet. The same reaction of neodymium chloride to neodymium nitrate in water results in the bands being made broader and more diffuse, and in some cases these bands are slightly shifted towards the red.

It must be stated that the study of the changes that take place in the neodymium bands has been too complicated for the present research. No other element shows such an extremely wide diversity in the structure of its various groups of bands, and at present no examples have been found where any bands can be traced throughout chemical reactions. The changes seem rather to be connected with a change in the relative intensity of bands in the same group, and, therefore, a shifting of the center of gravity of the absorption of the group itself. This may be true also of the uranyl bands, since it is known that the uranyl bands break up into much finer bands at low temperatures. At any rate, the changes in the uranyl bands at ordinary temperatures, when chemical reactions take place, are comparatively simple compared with the same changes in the case of the neodymium bands.

It is very important that a careful study be made of a series of chemical transformations of neodymium salts (especially at low temperatures). For instance, it has been shown that different anhydrous neodymium salts possess very different absorption spectra. Comparisons between the spectrophotographs of dry chemical reactions should be made and these compared with the same reactions in various solvents. As soon as we know what physical and chemical conditions are connected with given spectroscopic changes, then a study of the absorption spectra of crystals should be of aid in giving us an insight into the physical and chemical conditions within crystals. An example of this kind of study might be found in the different varieties of ice. Tammann[1] has shown that there are four distinct varieties, ice I and IV being lighter than water, and ice II and III being denser. According to Tammann the latter two varieties are composed of the simpler molecules. These different forms of ice are produced at different temperatures and pressures. The freezing-point of ice I is

$t°$	$-5.53°$	$-10.42°$	$-15.66°$
p	675	1141	1597 kg./cm.^{2}

Whereas ice III is formed by compressing to 3000 kg./cm.^{2} and cooling to $-80°$, ice II is formed by cooling to $-80°$ and then compressing to 2700 kg./cm.^{2} Ice IV is probably identical with the tetragonal ice observed by E. Nordenskiöld[2] or with the regular ice crystals formed from 75 per cent alcoholic solutions.[3] The absorption spectra of colored salts like those of neodymium, samarium, or uranium would probably aid in a study of these different crystalline types.

Another subject that seems to be of interest and promise is the possibility of breaking up absorption spectra into related groups. The work of Wood on sodium vapor has been very successful in this respect, each monochromatic stimulating wave-length exciting a certain resonating system within the atom or molecule, the resultant resonance spectrum including light of the same wave-length as that of the exciting light.

Among the rare earth elements praseodymium, neodymium, samarium, europium, terbium, dysprosium, and erbium show characteristic absorption spectra in the visible wave-lengths, and also are examples of excellent phosphorogens. Lanthanum, gadolinium, and yttrium do not possess absorption spectra, and only act as diluents. Following are some tables given by Urbain of the various phosphorescent spectra studied by him:

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[1] Zeit. phys. Chem., **72**, 609 (1910).
[2] Ann. d. Phys., **114**, 612 (1861).
[3] Barendrecht: Zeit. phys. Chem., **20**, 240 (1896).

PHOSPHORESCENCE OF PRASEODYMIUM, NEODYMIUM, AND ERBIUM IN CALCIUM OXIDE.

Praseodymium.	Neodymium.	Erbium.
4875 vs.	3920 s.	4040 w.
4905 w.	3980 s.	4045 w.
4940 m.	3640 to 4130	4060 w.
4985 to 5030 vw.	4190 sn.	4085 s.
5090 to 5130 vw.	4220 sn.	4095 m.
5170 m. dif.	4230 sn.	4460 m.
5225 to 5280 vw.	4270	4520 m.
5335 to 5370 w.	4295 vs.	4550 s.
5527 w.	4400 w.	4590 s.
5560 to 5600 w.	4515 w.	4620 w.
5790 w.	4575 s.	4670 m.
6045 s.	4610 w.	4690 m.
6065 s.	4660	4730 w.
6130 to 6220	4690 w	4760 m.
6260 vs		4785 w.
6340 s.		5270 to 5355 m.
6670 to 6800 dif.		5495 to 5550 w.
		5595 to 5630 m.

vs. = very strong; w. = weak; m. = medium; dif. = diffuse; vw. = very weak; s. = strong; sn. = strong and narrow.

The phosphorescence of compounds of the rare earths in other diluents is much simpler than in calcium oxide:

PHOSPHORESCENCE OF PRASEODYMIUM IN CALCIUM SULPHATE.

λλ 5876, 6000, and 6100.

PHOSPHORESCENCE OF ERBIUM IN CALCIUM SULPHATE.

λλ 5220, 5435, 5535.

PHOSPHORESCENCE OF ERBIUM IN CALCIUM FLUORIDE.

λλ 5170, 5200, 5250, 5310, 5400, 5465 strong, 5510 strong, 5620.

By using monochromatic light or homogeneous cathode rays of different velocities, it might be possible to excite only certain related bands and not the whole absorption spectrum. This might apply especially to the uranium salts. On the other hand, the presence of the diluent might preclude any possibility of this kind. The recent work of Wood and Franck[1] on the effect of the presence of helium on the resonance of iodine vapor would lead to a conclusion of this kind. A study of the fluorescence of sodium, potassium, mercury, and iodine vapor shows that the intensity of the emitted light is greatly reduced if air or some other inert gas is present. The effectiveness of a gas in destroying fluorescence appears to increase with the molecular weight. In the case of the fluorescence of anthracene, Elston found that hydrogen and nitrogen had very little effect, while oxygen and carbon dioxide had a very great effect.

Warburg[2] has shown that the current obtained from the negative point discharge is much greater in nitrogen, helium, argon, and hydrogen when the last traces of oxygen[3] have been removed. To explain this Warburg assumed that the mobility of the negative ions in the pure gases was much greater than when traces of oxygen were present. In other words, the electrons existed largely in a free condition, and as soon as oxygen was introduced, the electrons and negative ions were supposed to condense on the oxygen molecules. Small traces of the less electro-negative gases are found to act in the same way. Similarly, Franck and Wood believe that the more electro-negative elements have a greater power to destroy fluorescence, and this agrees with the relative destructive power as given by the series hydrogen, air, carbon dioxide, and ether vapor, the latter having the greatest effect. The conclusion reached is that the gases that interfere with the motions of the free electrons are also the ones that modify the motion of the bound electrons to the greatest extent. In this connection the influence of the presence of helium, argon, nitrogen, oxygen, and chlorine on the fluorescence of mercury and iodine has been studied.

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[1] Phil. Mag., 21, 309, 314 (1910).

[2] Ann. d. Phys., 40, 1 (1896).

[3] J. Franck: Verh. der deutsch. phys. Ges., July (1910).

According to Lorentz's hypothesis that the damping results from collisions, the damping factor would be a function of the molecular weight. On the other hand, the destructive effect of helium on the fluorescence of iodine is much less than that of hydrogen, the effects due to hydrogen and argon being about the same, although the molecular weight of the latter is forty times as great as the former. The gas having the greatest effect is chlorine, and next to it ether. It therefore seems that the power of a gas to combine with electrons is a very important factor in determining the rôle which that gas will play in the suppression of fluorescence.

The fact that the maximum intensity of fluorescence in a pure gas occurs at different pressures for different gases may also be explained on the above hypothesis. To obtain visible fluorescence there must be a sufficient number of molecules present to give a certain intensity of the emitted light, but this number of molecules must not be so great as to disturb each other. In a strongly electro-negative gas the vibration of electrons in one molecule will be influenced by the presence of other molecules in the neighborhood, so that for a gas like bromine the fluorescence would be expected to take place at much lower pressures than is the case for a much less electro-negative gas like iodine; while in the case of mercury the pressure would be very much greater. This has been found to be the case.

In treating the following cases of chemical reactions, the theory of aggregates, as fully developed in the general remarks at the end of this monograph, will be assumed. It may be possible to obtain some knowledge of these aggregates by other methods. In the study of α, β, and γ rays it is found that, in general, the absorption of these radiations depends on the atomic structure of the matter they traverse, rather than on the molecular structure. There may possibly be some exceptions to this rule. For instance, uranium and thorium salts emit α rays, the α rays probably coming from the uranium and thorium atoms themselves, before they break down into the next radio-active product. If one had a very thin layer of a uranium or thorium salt, it would be expected that the range of most of the α particles would be less if the uranium or thorium existed as an aggregate or in the simple molecular condition. It might, therefore, be found that the range of the α particles from uranyl nitrate would be related to the wave-length of the uranyl or uranous absorption bands. Knowing something of the electromagnetic forces necessary to alter the path of the α particles, it might be possible to find some of the properties of the fields of force that exist in the neighborhood of the uranium and thorium atoms, and the correlated effects upon the frequency of the absorption bands. Similar effects might be obtained in the case of the β and γ rays. The particles of the active deposits might also be used as nuclei about which aggregates would be formed.

Another possible method of studying aggregates is by the phosphorescence produced by α and β rays. The effect of changes in temperature could also be taken up in this connection. Several workers have concluded that the phosphorescence produced by the bombardment of certain kinds of screens by α rays is not due to the breaking up of crystals along lines or planes of cleavage, but that it is due to the breaking up of aggregates that are of approximately molecular dimensions; and that unless such aggregates are present, no phosphorescence is produced. For example, pure zinc sulphide is not phosphorescent, but when there are impurities present phosphorescent scintillations can be produced. It is probable that in most phosphorescent screens there are a large number of active centers present. When the centers on the surface are destroyed, those farther in the screen will become sources of scintillations. When the screen is new, each bombarding α particle probably excites a considerable number of centers. As the bombardment is continued the number of centers excited by each α particle decreases, although each particle will excite one or more centers, so that only the intensity and not the number of scintillations is decreased. The calculated diameters of the active centers of zinc sulphide and willemite are of molecular magnitude, whereas, in the case of barium platinocyanide, the diameter is about a hundred times this size. Marsden[1] has found that the number of scintillations is slightly less at 100° than at 15°.

It would be interesting to prepare salts so that various solvates and aggregates would be found, and then study the scintillations produced by them. The above suggestions are made since they are along somewhat different lines than those usually followed in the study of solutions.

NEODYMIUM CHLORIDE IN ETHYL ACETATE AND ANTHRACENE.

It was supposed by the older writers on the absorption spectra of solutions, that if two colored salts were dissolved in the same solution the frequencies of the absorbing centers of the one salt would be modified by the presence of the other salt, if the frequencies of the absorbing centers of the latter were almost the same as those of the former. Several attempts have been made to test this theory by experiment, but thus far no case is known where such an effect is shown, at least by the inorganic salts.

According to our theory of aggregates we would hardly expect any two absorbing centers to have any mutual effects on each other, unless both centers were part of the same aggregate. It is, however, quite difficult to find any solution containing such aggregates; indeed, it is doubtful if there are any that contain absorbing centers that have bands in the same region of the visible part of the spectrum. This line of work seems to be much more promising in the infra-red.

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[1] Proc. Roy. Soc., 84, A, 548 (1910).

It is known that, in the ultra-violet, anthracene and the neodymium salts have absorption bands that are near together. It was, therefore, hoped that a neodymium salt dissolved in anthracene would form aggregates containing both of these compounds, and that the resultant absorption spectrum would not be simply the superposition of the two separate absorption spectra of the given neodymium salt and anthracene. Unfortunately, the neodymium salts that were tried were not soluble in anthracene, and it seems, therefore, unlikely that we obtained aggregates containing both salts. Nevertheless, some spectrograms were taken with this idea in mind. Neodymium nitrate and anthracene are both soluble in ethyl acetate, and several solutions containing these three substances were prepared. It was found that only very dilute solutions of anthracene allowed the ultra-violet part of the spectrum to be transmitted, and no good photograph was obtained that showed the anthracene and neodymium nitrate ultra-violet bands on the spectrogram. It would seem very doubtful that any effect would be obtained, because of the improbability of anthracene and neodymium nitrate being contained in the same aggregate.

A and *B*, plate 11, give the absorption spectrum of neodymium nitrate and anthracene dissolved in ethyl acetate. In these spectrograms the ultra-violet absorption is so great that none of the anthracene bands are shown. *A* and *B*, plate 12, represent neodymium nitrate and anthracene in ethyl acetate. The lower strip of *B* shows several of the ultra-violet bands of anthracene, but does not show any of the neodymium ultra-violet bands. The upper strip of *B* shows the neodymium bands quite clearly, and also the very great general ultra-violet absorption. It is hoped that this effect can be satisfactorily tested with reference to the theory of aggregates, especially in the infra-red.

THE URANYL AND URANOUS BANDS.

The uranyl bands are usually ten or twelve in number and, starting at about λ 5000, have been designated by the letters *a*, *b*, *c*, etc., and form a series, the head band being the *a* band. The uranous bands appear throughout the spectrum and do not form any series. The uranous bands are characteristic of the uranous salts, and spectrograms of the absorption spectra of a uranous salt gradually oxidized into a uranyl salt by the addition of hydrogen peroxide show the complete independence of the two spectra.

A problem of considerable interest, and one that seems capable of solution, is the complete correlation of the *a*, *b*, *c*, . . . bands for the various uranyl salts in each solvent. For most solvents the uranyl bands of the different uranyl salts are very much alike. In aqueous solutions the differences are very marked, but by taking spectrophotographs of the transformation of one salt into another salt[1] Jones and Strong have succeeded in obtaining many relationships of this kind. By extending the work to low temperatures, and to the partly overlapping phosphorescent band spectra, it ought to be possible to connect continuously the various changes that these bands undergo.

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[1] Publication 130, Carnegie Institution of Washington.

OXIDIZATION OF URANOUS TO URANYL SALTS IN SOLUTION.

Some spectrophotographs have been made of the formation of a uranous salt from a uranyl salt by the nascent hydrogen reduction method. These spectrograms are somewhat unsatisfactory, since there is a considerable amount of gas, opaque residues, etc., formed, and the reduction takes a considerable length of time. It is hoped in the future that this reduction may be produced by the action of occluded hydrogen (for example in palladium) that will be liberated on being heated, or by some other method that will not require the addition of other acids or salts.

The reverse process of the oxidization of uranous salts in solution is a very satisfactory one, and the spectrograms can be photographed very well indeed. This method simply consists in the addition of a small amount of hydrogen peroxide to the uranous solution. The spectrophotography of these reactions, as already mentioned, has furnished an admirable method by means of which the uranyl and uranous bands can be completely separated. Several oxidizing agents have been added to aqueous and alcohol solutions of uranous salts that showed both the water and alcohol bands, in order to see whether there is any selective oxidation.

OXIDIZATION OF URANOUS CHLORIDE BY HYDROGEN PEROXIDE.

The first solution of uranous chloride to be oxidized, in order to compare the effect of the presence of acid and of other salts, was that of the very intensely colored solution of uranous chloride formed by reducing an ether solution of uranyl chloride. To one part of this solution were added four parts of water, and this required for oxidization about a one-fourth part of a solution of hydrogen peroxide. A cloudy and semi-transparent precipitate was formed during oxidization. When one part of the ether solution of uranous chloride was added to six parts of concentrated hydrochloric acid, the resultant liquid contained a cloudy precipitate. The addition of a few drops of hydrogen peroxide clarified the solution, but it required over two parts of hydrogen peroxide before the uranous chloride was completely oxidized. Following are the tabulated results of these experiments:

Parts uranous chloride solution.	Parts of solvent added.	Parts hydrogen peroxide in water necessary for oxidization.
1.0	4.0 water	0.6
1.0	6.0 hydrochloric acid. Soluble.	2.0
1.0	12.0 $AlCl_3$ in water. Small precipitate	0.7
1.0	6.0 Conc. HNO_3. Only partly oxidized	3.0
1.0	10.0 acetic acid. Precipitate formed	0.7
1.0	12.0 ethyl alcohol	0.5
1.0	12.0 glycerol	0.7
1.0	12.0 methyl alcohol. Precipitate formed	0.6
1.0	12.0 $Ca(NO_3)_2$ in $2H_2O$ and $3CH_4O$. Precipitate	0.4
1.0	90.0 ethyl alcohol	0.6
1.0	12.0 water, 4.0 $NaClO_4$ in water, and HCl.	1.5

A solution of uranous chloride in water was prepared in the usual manner, and made strongly acid by the addition of hydrochloric acid, in order to increase the stability of the solution. Solutions of uranous salts sometimes form precipitates on standing. Uranous chloride was dissolved in the following solvents, and mixed with the following compounds:

Parts uranous chloride solution.	Parts of solvent added.	Parts of hydrogen peroxide necessary for oxidization.
1.0	10.0 water	0.2
1.0	10.0 ethyl alcohol	0.2
1.0	10.0 glycerol	0.35
1.0	10.0 hot water	0.2 precipitated.
1.0	10.0 water + H_2SO_4	0.1
1.0	10.0 acetic acid	0.2
1.0	10.0 acetone	0.2 precipitated.
3.0	10.0 nitric acid	2.0
1.0	10.0 calcium nitrate in $2H_2O+3CH_4O$	0.2
1.0	10.0 hydrochloric acid	2.0
1.0	10.0 aluminium chloride in water	0.25
1.0	10.0 sodium perchloride in water	0.2
1.0	10.0 aluminium chloride in hot water	0.16
1.0	7.0 hot hydrochloric acid	0.8
3.0	8.0 hot nitric acid	0.0 NO_2 formed.

A spectrogram was made showing the effect of the addition of hydrogen peroxide to a solution of about 0.75 normal concentration of an aqueous solution of uranous chloride. The uranous chloride solution did not show any uranyl bands at all, and even when the uranous bands appeared very strongly there was very little absorption in the region from λ 3500 to λ 4200. The edges of the uranous bands were well defined, there being four very strong bands extending between the following limits: λ 4250 to λ 4400, λ 4700 to about λ 5080, λ 5400 to λ 5600, and λ 6100 to λ 6800. The transmission between these bands was quite strong and appeared to be uniformly distributed.

The addition of hydrogen peroxide caused the uranous bands to decrease in intensity. As far as the quite sharp uranous bands are concerned it seems that the individuality of these bands decrease at about the same rate; but the λ 4340 band is replaced by the blue-violet uranyl band, and the λ 5500 band is also apparently replaced by wide general absorption in this region, extending 500 or 600 Ångström units. On the other hand, the transmission seems to be pretty complete in the red and, with the exception of the very weak uranyl bands, in the region λ 4500.

A, plate 44, represents the effect of the addition of hydrogen peroxide to a solution of uranous chloride in water, acetone, and hydrochloric acid. The solution did not contain the right proportion of the solvents to show the fine structure of the uranous and uranyl bands brought out by some acid acetone solutions. The spectrogram shows very clearly the various uranous bands, and how they are replaced by the uranyl bands as hydrogen peroxide is added.

The band that appears at about λ 4970, and is quite strong on several of the strips, is a uranous band, and disappears when sufficient hydrogen peroxide is added. In the upper strip, which represents the absorption of the uranyl salt, there is a wide, very diffuse and weak region of absorption, running from about λ 5000 to λ 5100.

In addition to the ordinary uranous and uranyl bands, there is a weak band about 15 Ångström units wide at about λ 5080. This band appears best in the central strips, and can hardly be detected at all in the lowest and highest strips. It is, therefore, difficult to say whether it is a uranyl or a uranous band. In fact it may not be due to either of the two uranium salts. The band is very similar to the one described under the oxidization of uranous chloride in hydrochloric acid, only with the exception that the bands have very different wave-lengths.

OXIDIZATION OF URANOUS CHLORIDE IN HYDROCHLORIC ACID BY HYDROGEN PEROXIDE.

It seems that the acid uranous aggregates are in general more stable than the neutral aggregates. Hydrogen peroxide oxidizes the strongest acid solutions. A spectrogram was, however, made of a neutral uranous chloride solution, to which a large amount of concentrated hydrochloric acid had been added, and to which increasing amounts of hydrogen peroxide were added. The addition of the hydrochloric acid caused the uranous chloride bands to be shifted about 100 Ångström units towards the red. In other respects the bands were not greatly changed, with the exception of the bands in the red.

The uranous bands, on the addition of hydrogen peroxide, gradually decreased in intensity without having their wave-length changed. At the same time the uranyl bands appeared and, as is the case for strongly acid solutions, the uranyl bands appeared quite sharp and intense.

It may be supposed that in the case of the existence of acid aggregates it would require a longer time for the oxidization to take place than in the case where only neutral aggregates are present. It would be interesting to know what the reaction velocities of these oxidization reactions are for the various kinds of aggregates.

It is a difficult matter to preserve uranous nitrate in the uranous condition. When uranyl nitrate is mixed with nitric acid and zinc is added, some uranous nitrate is formed, but it is soon re-transformed into the uranyl condition. This would indicate that uranous nitrate in water containing nitric acid is unstable and is quickly oxidized. On the other hand, uranous chloride can be mixed with concentrated nitric acid and the uranous absorption spectrum will be found to be entirely different from that of uranous chloride. In this case the uranous salt will remain as such for at least a day or two when kept at room temperatures. This may be explained by supposing that the nitric acid aggregate of uranous nitrate is much more stable than the salt itself.

According to the law of mass action, if a nitrate is mixed with uranous chloride, some uranous nitrate ought to be formed. To test the stability of uranous nitrate, uranous chloride was dissolved in a solution of calcium nitrate in water and methyl alcohol. Under these conditions both "water" and "alcohol" bands appeared. This solution did not oxidize, but a black precipitate was formed. This experiment could also be explained by supposing that the uranous nitrate in this solution existed in the condition of some kind of an aggregate. The precipitate formed appeared to be similar to that which is formed on heating a neutral uranous salt to the boiling-point.

Uranyl chloride, hydrochloric acid, and potassium nitrate were mixed in water and methyl alcohol, and zinc was added. The reduction took place easily and the resulting uranous salt remained stable. It is probable that in this case, also, more stable aggregates than neutral uranous nitrate were formed. As a reciprocal reaction, uranyl nitrate, aluminium chloride, and hydrochloric acid (in small quantity) were dissolved in water and zinc added. A stable solution of a uranous salt, probably largely chloride, was formed. In this case very little uranyl nitrate existed in the solution after the aluminium chloride and hydrochloric acid were added. These three experiments would then indicate that there is probably but little oxidization of uranous chloride to the uranyl salt under these conditions.

THE OXIDIZATION OF URANOUS SULPHATE.

The preparation of concentrated aqueous solutions of uranous chloride and uranous bromide is not difficult, using the method of reduction of the corresponding uranyl salt with nascent hydrogen. A concentrated aqueous solution of uranous sulphate can be obtained in a similar manner, but on standing almost all of the uranium is precipitated. The presence of sulphuric acid, however, enabled us to prepare a far more concentrated solution of uranous sulphate, and this was quite stable.

A solution of uranous sulphate was prepared by reducing uranyl sulphate with nascent hydrogen. The precipitate formed was partly dissolved in water. The aqueous solution of uranous sulphate thus prepared was approximately 0.1 normal, and was fairly stable when kept in ground-glass stoppered bottles. When exposed to the air it oxidized slowly to the uranyl condition. The addition of methyl alcohol, ethyl alcohol, or acetone to the aqueous solution of uranyl sulphate precipitated some of the salt.

A spectrogram, *B*, plate 35, shows the oxidization of an aqueous solution of uranous sulphate to uranyl sulphate, by the addition of an aqueous solution of hydrogen peroxide.

The original film shows quite a large number of the uranyl bands. The wave-lengths of the uranyl bands seem somewhat greater than those of uranyl sulphate solutions made from the chemically pure salt. This is probably due to the presence of a considerable amount of zinc sulphate. In addition to the regular uranyl sulphate bands there is present quite a fine and weak band at λ 5100. This band does not seem to vary to any considerable extent from strip to strip, and it is difficult to say whether it is a uranyl or a uranous band.

THE OXIDIZATION OF URANOUS BROMIDE BY HYDROGEN PEROXIDE.

An aqueous solution of uranous bromide is oxidized by hydrogen peroxide in the same way that uranous chloride is oxidized. The absorption spectra of the bromide and chloride are quite similar for the uranyl and the uranous salts.

A solution of uranous bromide in ethyl alcohol is oxidized by hydrogen peroxide. In the case photographed the alcoholic solution had a very great ultra-violet, violet, and blue absorption after the oxidization had taken place.

B, plate 44, represents the oxidization of a glycerol solution by the addition of hydrogen peroxide. In addition to a few of the uranyl bands, the characteristic uranous glycerol bands consist of a wide diffuse band at λ 4400 and a strong and quite persistent band at λ 4680. This is about the most persistent band in the uranous spectrum, although in the lower strip it is only about 40 Ångström units in width, while the red band is about ten times as wide. The bands λλ 4400, 5000, and 5250 are very much alike, being about 100 Ångström units in width, very weak and diffuse. The band λ 5000 is apparently double. The red band is quite strong, running from λ 6050 to λ 6400. It is accompanied by a very weak band at λ 6600. This band is extremely weak, and probably corresponds to the water band in the same region. The addition of hydrogen peroxide simply causes each one of these bands to decrease in intensity, while the uranyl bands increase in intensity.

A POSSIBLE METHOD OF MEASURING THE STRENGTHS OF ACIDS.

Several methods have been employed for measuring the relative strengths of acids. Among these are: The power of acids to divide a base between them, as determined by thermo-chemical and volume-chemical methods; their power to invert cane-sugar; to saponify an ester; to convert acetamide into ammonium acetate; their conductivity, etc. All of these methods measure the relative concentrations of the hydrogen ions in the solutions of the various acids, the degree of dissociation determining, of course, the relative strengths of acids. All acids at infinite dilution, or when completely dissociated, are, then, of the same strength. In more concentrated solutions the strengths of acids vary directly as their dissociation. Our work on absorption spectra has shown that the positions of the uranyl and the uranous bands for different uranium salts are often quite different. We could add just enough of the acid in question to transform completely the original salt into the salt of the acid in question, and then express the concentration of the acids and salts in gram molecules per liter, or by any other convenient method.

Some spectrograms of this kind have been made indicating the relatively great strength of hydrochloric acid. As yet, however, the subject has only been touched upon. It is important that an accurate quantitative method for measuring the intensity and wave-length of the bands be first devised. There will be one obstacle that may cause some difficulty in this method, and that is the presence of the acid (above, the acetic acid) displaced from the colored salt by the addition of the acid to be tested.

Experiments of this kind should be carried out with various uranyl, uranous, and neodymium salts, etc., in different solvents, to find whether the relative strengths of acids are the same for the various colored salts, for the different solvents, for different concentrations, for different temperatures, for salts when in the presence of colorless salts, etc. Spectrophotography of this kind only includes a study of the spectra as they are changed from that of one neutral salt to that of another. Such a method, however, could hardly be made as accurate a measure of the strength of acids as the conductivity method, and not nearly so general.

ARE THE IONS FACTORS IN THE ABSORPTION OF LIGHT?

It is one of the remarkable facts brought out in this investigation, that ions as such do not seem to play any rôle in the absorption of light. If the ions were the absorbers of light in solution, then the absorption spectrum of a solution would vary with the dilution of the solution, since the dissociation of a solution varies with the dilution.

There are solutions of the different colored salts of a certain metal, for which the wave-lengths of the absorption bands are different. It will be remembered in the case of neodymium that the absorption spectra of the acetate, chloride, and nitrate are quite different from one another. The spectra of these salts should all be the same, in dilute solution, if the absorption of light were due solely to the ions.

Jones and Guy are now studying very dilute solutions of certain salts, to see whether there is any detectable difference between the spectrograms in very dilute and in more concentrated solutions.

There are not many cases known where the wave-lengths of the absorption bands of different salts of the same metal in the same solvent are very different. Uranyl nitrate in water, however, gives bands that are of quite different wave-lengths from those given by other uranyl salts in water. The following will illustrate this point:

	a	*b*	*c*	*d*		*f*
Uranyl nitrate.....	4870	4705	4550	....	4310	4155
Uranyl sulphate....	4900	4740	4580	4460	4330	4200

While previous work of Jones and Strong[1] indicated that there was little or no change in the positions of the nitrate and sulphate bands with change in concentration, recent experiments made with the concentrations 0.5 and 0.003 normal indicate that in the more dilute solutions the sulphate bands have been slightly shifted towards the violet, while the nitrate bands have been slightly shifted towards the red. It may be possible that, with sufficient dilution, the sulphate and nitrate bands would occupy the same position, as would be the case if the ions were the only absorbers in the solutions; yet the shifts are so small with the dilution that this seems improbable.

Indeed, it has recently been shown by Jones and Guy, working in very dilute solutions and with a depth of layer of 250 cm., that the uranyl nitrate bands are only very slightly shifted towards the red, and the uranyl sulphate bands are only very slightly shifted towards the violet. The evidence is therefore convincing that the presence of the NO_3 and the SO_4 groups influences the periods of the absorbing centers in the uranyl atoms or groups. Another good example that can be tested in a similar way is that of uranyl chloride and uranyl nitrate in acetone. These uranyl bands are quite strong, and the difference in the wave-lengths of corresponding bands is at least from 50 to 60 Ångström units.

Uranyl nitrate in acetone.....	4840		4665		4515
Uranyl chloride in acetone.....	4960 4935	double	4765 4795	double	4610

Such facts as the above can be readily explained in terms of the theory of aggregates. A uranyl nitrate aggregate loses an NO_3 group, and becomes an ionized aggregate or complex ion. The loss of the NO_3 group causes a decrease in the hypsochromous effect, but this would be smaller if the aggregate were large. There would be a similar result in the case of the uranyl sulphate aggregates. It is, however, surprising that these aggregates, if they exist, are not broken up when the solution becomes very dilute.

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[1] Proc. Amer. Phil. Soc., 48, 192 (1909).

It is important that acid aggregates should be studied in the same way. It is possible that these would break up more easily with increase in dilution than the neutral aggregates apparently do.

THE OXIDIZATION OF URANOUS SALTS BY NITRIC ACID.

On account of the very great instability of uranous nitrate, it was expected that the addition of concentrated nitric acid to aqueous solutions of the other uranous salts would cause their rapid oxidization. In the case of uranous bromide, bromine was given off. In general, the addition of nitric acid to an aqueous solution of uranous chloride causes the oxidization of that salt, but if a large amount of nitric acid is added, the solution changes from a very deep green to a light greenish-yellow, and the absorption spectrum shows that there is still a very considerable amount of uranous salt in the solution; and the bands are quite different from those of neutral uranous chloride. This uranous solution will remain for days, and seems to be quite stable.

A, plate 45, represents the absorption of a solution of uranous bromide in water and methyl alcohol to which dilute nitric acid is added in increasing amounts. The addition of the nitric acid caused a slight increase in the transmission in the ultra-violet, but this was quite small. The uranyl bands appear, but are very weak. In strip 1 there is a band running from λ 4200 to λ 4400. This is probably due to a water and alcohol band, the alcohol band being on the red side. Apparently the alcohol band disappears, since the band narrows rapidly on its red side, and then decreases slowly in intensity. The alcohol band at λ 4650 has practically disappeared in the third strip. In strip 1 there is a weak, very diffuse band at λ 4800, and a strong band at about λ 4950. As nitric acid is added these bands are replaced by a wide and strong region of absorption, running from λ 4600 to λ 5000. The band λ 5200 disappears. The band λ 5500 is shifted about 150 Ångström units towards the violet. The alcohol band running from about λ 6000 to λ 6300 narrows rapidly on its short wave-length edge, disappears, and is replaced by a weak, diffuse band at about λ 6100. The red water bands increase and then gradually decrease in intensity. When this decrease begins, the long wave-length band is much the stronger of the two and indicates that the uranous bromide alcoholate and the uranous bromide hydrate have both been changed to some uranous nitrate hydrate, and that this compound is then oxidized to the uranyl salt.

The addition of nitric acid to the aqueous solution of uranous sulphate previously described produces a slow oxidization of the uranous into the uranyl salt. This oxidization requires several minutes and would be a very good reaction with which to study reaction velocity, the intensity of the absorption bands being determined by a radiomicrometric method. *B*, plate 46, is a spectrograph of the oxidization produced by adding nitric acid to an aqueous solution of uranous sulphate. Strip 5 is the absorption of the same solution as that shown by strip 4, the only difference being that the solution had been allowed to stand for several minutes.

In the solution of uranous sulphate oxidized by nitric acid, the uranyl bands are shifted slightly towards the violet, compared with the uranyl bands of the uranous sulphate solution oxidized by hydrogen peroxide, showing that probably some uranyl aggregate is formed that contains some NO_3 groups.

The addition of the first amount of nitric acid causes the transmission in the ultra-violet to be increased very greatly, with the appearance of a large number of the uranyl bands. In the red the wide uranous sulphate band is decreased in intensity. Strips 2 and 3 show the narrow red sulphate water band, but in strip 4 this band has completely disappeared and is replaced by a single weak band 300 Ångström units wide.

B, plate 45, represents the change in the absorption spectrum of a solution of uranous chloride in methyl alcohol and acetone, to which nitric acid is added. This spectrogram shows the rapid disappearance of the alcohol bands. The various uranous bands seem to be replaced by the bands of some hydrate of a uranous nitrate aggregate, and this aggregate is then gradually oxidized. The ultra-violet transmission increases until the last strip, which shows a very great increase in the ultra-violet absorption. The last strip still shows the presence of a considerable amount of uranous salt, and the absorption bands are entirely new.

A, plate 37, represents the absorption spectrum of uranous chloride as it is gradually changed into uranous nitrate by the addition of nitric acid. *B*, plate 37, represents the corresponding changes in the absorption spectra that take place, when to a solution of uranous chloride in equal parts of water and methyl alcohol is added nitric acid also dissolved in equal parts of water and methyl alcohol. The upper strip represents the absorption of the resultant uranyl salt after oxidization with hydrogen peroxide. As the bands are quite wide and strong most of the changes can be seen on the plate itself. It will be seen that the absorption spectrum of the nitric acid solution of uranous chloride is very different from that of the neutral chloride. This spectrogram also seems to indicate that there is not a gradual shifting of the chloride bands into the nitrate bands, but in the case of the λ 6300 chloride band there is a decrease in intensity without being shifted; and this is replaced by the uranous nitrate band at about λ 6100. *B* shows that the addition of nitric acid results in a rapid and almost *complete disappearance of the alcohol bands, while the uranous nitrate water bands increase in intensity.*

URANOUS ACETATE AND THE EFFECT OF THE ADDITION OF NITRIC ACID.

The reduction of uranyl acetate to the uranous salt is not complete, and a precipitate was formed, so that the resultant solution here used was quite dilute. A spectrogram (*B*, plate 36) was made of this solution, and the first four strips represent the absorption of layers of different thicknesses, for the last layer this being about 20 cm. To this solution were added 10, 20, and 40 drops of concentrated nitric acid, the absorption being represented by strips 6, 7, 8. The first five strips represent quite well the absorption of uranous acetate, and they also show very clearly the uranyl acetate bands. The addition of nitric acid causes a great increase in the general transmission throughout the spectrum, and a very rapid decrease in the intensity of the uranous bands. The resultant uranous bands are, of course, those of uranous nitrate. This spectrogram shows that uranous acetate is quickly oxidized in the presence of nitric acid, whereas this is not the case with uranous chloride.

THE SELECTIVE ACTION OF CHEMICAL REAGENTS ON SOLVATES.

After photographing the effect of oxidizing the uranous salts to the uranyl condition by the addition of hydrogen peroxide, it was natural to study what effect the addition of other oxidizating agents would have upon the various solvate bands. It will be remembered that the addition of hydrogen peroxide caused the complete oxidization of the various solvates in the solution. It was found that the action of the other oxidizing agents used was, in general, of a more or less selective nature.

A, plate 47, represents the absorption of a solution of uranous bromide in 3.5 parts water and 6 parts methyl alcohol, to which was added calcium nitrate in methyl alcohol, 1.2 normal.

	Uranous bromide (amount constant).	Drops of calcium nitrate in methyl alcohol.	Percentage water in solution.
Strip 1......	....	0	37
Strip 2......	...	10	33
Strip 3......	....	20	28
Strip 4......	....	40	21
Strip 5......	....	80	14

The addition of calcium nitrate causes a very great increase in the amount of the general absorption of the short wave-lengths. This is to be especially noticed in the last addition of the calcium nitrate. The most important thing to be seen from this spectrogram is the rapid and almost total disappearance of the water bands. The intensity of the alcohol bands changes very little, if any, and it seems quite improbable that the uranous hydrate could have been converted into uranous alcoholate without the alcohol bands increasing very much in intensity. The natural conclusion is that the uranous hydrate has been oxidized to the uranyl condition by the calcium nitrate. The original film shows that in the third strip the two red uranous water bands have almost the same intensity. This may mean that the uranous bromide has been changed to some other salt.

B, plate 47, represents the absorption of a solution of uranous bromide in 2 parts of water and 3 parts of methyl alcohol, the resultant solution being about 0.12 normal. To this were added small amounts of a solution of sodium perchlorate in methyl alcohol. It will be seen that the water bands decrease in intensity as the sodium perchlorate is added, and that the longest wave-length water band becomes more diffuse. The reason why the fifth strip is vacant is on account of the formation of a precipitate. The precipitate was not analyzed, but the spectrogram shows that the uranous hydrate has almost entirely disappeared from the solution, while there is still present quite a considerable amount of uranous alcoholate. This spectrogram is, therefore, a good example of a case of *selective precipitation of solvates*. *B*, like *A*, plate 47, indicates that there is a change in the constitution of the uranous hydrate before it was precipitated.

A, plate 46, represents the effect of the addition of potassium nitrate and calcium nitrate to a solution of uranous bromide. In strip 1 we have the absorption due to a solution of uranous bromide in 3.5 parts water and 6 parts methyl alcohol. To this is added a solution of potassium nitrate in 2 parts water and 3 parts methyl alcohol, which results in a precipitate. The precipitate was filtered off and the resultant solution gives the absorption as represented in strips 2 and 3. It will be seen that only the uranous hydrate has been precipitated. Strip 4 represents another solution of uranous bromide in 3.5 parts of water and 6 parts of methyl alcohol, and to this solution is added calcium nitrate dissolved in 2 parts of water and 3 parts of methyl alcohol. The effect of the addition of this calcium nitrate is to cause the almost complete disappearance of the water bands, while the intensity of the alcohol bands remains practically the same. In the fifth strip it will be seen that the long wave-length water band is nearly 150 Ångström units in width, and is very much wider than the other red water band. This spectrogram furnishes striking evidence in support of the view of the selective oxidization of the uranous hydrate in this solution.

A, plate 42, represents the absorption of uranous bromide in water and methyl alcohol to which an aqueous solution of calcium nitrate is added. The spectrogram shows the decrease in the intensity of the alcohol bands. This is most likely due to the increase in the percentage of water present in the solution. The second strip shows the very quick change in the relative intensity of the two red uranous water bands. This effect seems to be a general one for the addition of calcium nitrate to solutions of uranous chloride, bromide, or sulphate. The spectrogram does not seem to indicate that any of the uranous salt has been oxidized.

B, plate 41, shows that when hydrogen peroxide is dissolved in the same proportion of water and methyl alcohol as the uranous bromide, the alcohol and water bands both disappear at the same rate, indicating that hydrogen peroxide has no selective action on these two solvates.

The solution of uranous chloride used was acidulated with hydrochloric acid, and when mixed with an equal volume of methyl alcohol gave the water and methyl alcohol bands of about the same intensity. Two solutions were used: one (spectrogram *A*, plate 36) in which the alcohol bands were much the stronger, and the other (spectrogram *A*, plate 41) in which the water bands were slightly stronger. Calcium nitrate in 2 parts of water and 3 parts alcohol was added, the amounts being 10, 20, 40, and about 120 drops. The last strip of *A*, plate 41, represents the result of the addition of hydrogen peroxide. Spectrogram *A*, plate 38, represents the effect produced by adding sodium chlorate dissolved in equal parts of water and alcohol. In this case no oxidization resulted. *A*, plate 36, shows very little change in either the water or the alcohol bands. The red water bands have their relative intensity greatly changed, however, on the addition of calcium nitrate. *A*, plate 41, shows this same relative change in the intensity of the two red water bands. The spectrogram shows a very considerable increase in the intensity of the alcohol bands, and a decrease in the intensity of the water bands. *A*, plate 38, shows very little if any change at all in the absorption spectra. Even the red water bands remain of about the same relative intensity.

B, plate 38, represents the absorption of one part of uranous chloride in water to which one part of methyl alcohol is added. Succeeding strips, with the exception of the last, represent the effect of adding potassium chlorate in water and methyl alcohol. The last strip represents the effect of adding hydrogen peroxide. This spectrogram shows the almost complete disappearance of the water bands, while the alcohol bands remain of about the same intensity.

Plate 43, *A*, represents the absorption of uranous chloride in one part of water and one part of methyl alcohol. Hydrogen peroxide, in equal volumes of water and methyl alcohol, was added to this solution, three drops at a time; except to the solution whose spectrogram is shown in the last strip, twelve drops of hydrogen dioxide were added. The uranous alcoholate and hydrate are oxidized to the same extent.

Plate 43, *B*, represents the absorption due to uranous bromide 0.5 normal in water, to which three parts of methyl alcohol were added. After a time a precipitate was formed. This was filtered off, and strip 2 is the spectrogram of the solution. Successive strips represent the effect of adding increasing amounts of potassium chlorate in equal volumes of water and methyl alcohol. Very little, if any, relative action manifests itself.

A, plate 27, represents the absorption of concentrated nitric acid to which increasing amounts of uranous chloride were added.

B, plate 27, represents the absorption of the filtrate of a uranous bromide solution. A solution of uranous bromide of sufficient strength when mixed with alcohol to give the water and alcohol bands of the same intensity usually forms a precipitate if allowed to stand. Strip 1 shows the absorption of the filtrate of such a solution, and indicates the selective precipitation of the hydrate. The succeeding strips represent the absorption of uranous bromide in water and alcohol, to which is added nitric acid in the same proportion of water and alcohol. The last strip represents the solution containing the greatest amount of nitric acid, to which was added a few drops of hydrogen peroxide.

C, plate 27, represents the absorption of uranous chloride in propyl alcohol, to which acetone is added. *A* gives what we shall call the uranous nitrate spectrum, although it is probably quite different from that of a neutral aqueous uranous nitrate absorption spectrum. *B* is a good example of selective precipitation, and of the action of nitric acid in increasing the intensity of the hydrate bands at the expense of the alcoholate bands. *C* shows how the addition of acetone causes the almost complete disappearance of the uranous bands, and how, at the same time, the uranyl acetone bands appear in place of the uranous bands.

Plate 39, *A*, strip 1, represents the absorption of uranous chloride in equal parts of water and methyl alcohol. Strip 2, the same, to which is added a solution of sodium perchlorate in water and methyl alcohol. Strip 3 is a corresponding strip when sodium perchlorate is replaced by potassium chlorate in 1 parts of water and 3 of methyl alcohol. Strip 4 is the absorption of a solution of uranous chloride in methyl alcohol and ether. Strips 2 and 3 show quite a strong selective action of these salts in increasing the relative intensity of the alcohol bands. This action is especially marked in the case of potassium chlorate.

Plate 39, *B*, strip 1, represents the absorption of uranous chloride in equal parts of water and methyl alcohol, to which calcium nitrate is added; the latter being dissolved in 2 parts of water and 3 parts of methyl alcohol in strip 1; in 1 part water and 1 part methyl alcohol in strip 2, and in pure water in strip 3. Strips 4, 5, 6 represent the absorption of uranous chloride in equal parts of water and methyl alcohol, to which potassium nitrate is added; in strip 4, potassium nitrate is in 2 parts water and 3 parts of methyl alcohol, strip 5 in equal parts of water and methyl alcohol, and in strip 6 in pure water. The last strip represents the absorption of uranous chloride in equal parts of water and methyl alcohol. This spectrogram indicates that the action of the calcium and potassium nitrates may be that of driving back the amount of hydrate in equilibrium with the alcoholate, and that by increasing the proportion of water present in the solution the amount of hydrate present is increased at the expense of the alcoholate.

THE REDUCTION OF URANYL SALTS IN SOLUTION.

The reduction of uranyl to uranous salts deserves a thorough study, and undoubtedly offers a fertile field for investigation, and this partly on account of the light that quantitative spectrophotography will probably throw upon the subject. In certain solvents some interesting results have already been obtained. In the case of an ether solution of uranyl chloride it was found that, on the addition of zinc and hydrochloric acid, three phases resulted—an oily and extremely concentrated solution of uranous chloride formed at the bottom; a much more dilute solution of uranous chloride which was above the oily layer and which, on standing, gave up its uranous salt to the oily liquid below; and the upper layer, which only contained uranyl chloride in solution. These three liquid layers were completely separate from one another. When the whole system was thoroughly shaken and allowed to stand, the three strata soon separated again from one another.

Uranyl chloride dissolved in isobutyl alcohol, to which zinc and strong hydrochloric acid are added, also shows the formation of an oily and dense liquid, which was almost opaque on account of the large amount of uranous chloride dissolved in it. These very concentrated solutions of uranous salts would serve admirably for low-temperature work, and for the detection of the Zeeman effect.

When hydrochloric acid is added to a solution of uranyl chloride in propyl alcohol, the two solutions mix. Zinc is then added and the reduction takes place very slowly.

A, plate 26, represents the absorption spectrum of the uranous chloride solution in ether, to which some hydrochloric acid had been added. The absorption spectrum is quite characteristic, and shows some new bands. Several of these bands are quite sharp and narrow. As an example, there is a band near λ 5000 that is quite strong and is only about 25 Ångström units in width.

REDUCTION OF URANYL CHLORIDE IN METHYL ESTER.

To a solution of uranyl chloride in methyl ester were added hydrochloric acid and metallic zinc. The hydrochloric acid does not mix with the ester solution. For a considerable time hydrogen is given off, the ester solution remaining of a greenish-yellow color. Quite suddenly, however, the ester loses its greenish-yellow color and becomes slightly clouded, the solution being of a pale-white color. At the same time an almost black solution is formed, whose volume is about the same as that of the hydrochloric acid added. Further addition of hydrochloric acid results in the ester solution becoming of a darkish-green color, while a small amount of the very deeply colored, oil-like solution still remained at the bottom of the solution.

SELECTIVE REDUCTION OF URANYL AGGREGATES.

The method employed for the preparation of uranous salts for work on their absorption spectra has usually been to add an acid corresponding to that of the uranyl salt, and some zinc. There would be present in the solution of the uranous salt the corresponding zinc salt. It is possible, under these conditions, to obtain fairly concentrated solutions of uranous chloride, uranous bromide, and uranous sulphate. It does not seem, by this method, to be possible to obtain uranous nitrate in stable condition. A small amount of uranous nitrate is formed, but it is very quickly oxidized again. Dilute aqueous solutions of uranous acetate can be obtained by this method.

The most concentrated solution of any uranous salt thus far obtained is that of uranous chloride. A considerable volume of a solution of uranyl chloride in ether was prepared; to this was added a small amount of concentrated hydrochloric acid and zinc. The uranous chloride formed is nearly insoluble in the ether, and collects in a dark, oily liquid at the bottom of the vessel.

The action of certain acids on the uranyl salts is peculiar. As has been stated, the addition of nitric acid and zinc to a uranyl chloride solution did not result in the formation of any uranous salt, although the absorption spectra would probably have shown very little effect on the uranyl chloride bands produced by the addition of nitric acid. The sulphate would probably have been a better uranyl salt to use in this connection, because the uranyl sulphate bands are harder to change to the nitrate bands then the uranyl chloride bands are. To a uranyl chloride solution containing some free hydrochloric acid were then added, as before, some nitric acid and zinc. In this case some uranous salt was produced, but it was quite unstable and was quickly oxidized again.

On the other hand, to an aqueous solution of uranyl chloride were added some hydrochloric acid and zinc. A uranous salt was formed, but in a few minutes this was transformed back into the uranyl condition again. This is rather unexpected, since it would be thought that the uranous salt would be in the condition of the chloride, and the chloride is quite stable. To an aqueous uranyl nitrate solution were then added a large amount of concentrated hydrochloric acid and a little zinc. The solution turns green during the first few minutes and then goes over to the uranyl state, although hydrogen gas is being rapidly evolved. Very little could be done with the bromides along this line on account of the liberation of bromine. It would be very interesting to find how much the uranyl bromide bands are changed before the bromine gas is evolved, since this would give the condition of the aggregate when it is broken up and bromine evolved.

B, plate 25, is a spectrogram giving the result of the addition of a large amount of acetic acid and a little zinc to uranyl chloride dissolved in acetone. The chemical conditions in this solution are quite complex and, therefore, little can be said about them. The composition of the red uranous band is quite unique in this case. For a considerable amount of the solution the red band resembles that of the red glycerol band of uranous chloride. On decreasing the amount of salt the band breaks up into four very weak, diffuse bands, resembling more or less the aqueous uranyl chloride bands. The extreme red part of the absorption consists of a triplet with the central and strongest band located at about λ 6750. The other bands are approximately at λ 6670 and λ 6820. The uranyl bands are exceptionally strong, as will be seen from the spectrogram.

DIRECT SPECTROSCOPIC EVIDENCE FOR THE EFFECT OF MASS.

According to the law of Mass Action if the salts, uranyl chloride and calcium nitrate, were dissolved in water, uranyl chloride and uranyl nitrate would both be present in the solution. According to the theory of aggregates the addition of calcium nitrate should shift the uranyl chloride bands to the violet, while the addition of calcium chloride to uranyl nitrate should shift the uranyl nitrate bands to the red. This was found to take place.

Preliminary tests showed that the addition of calcium nitrate to uranyl nitrate caused a slight shift towards the violet. It appears, therefore, that calcium has very little effect, it being only the acid radicle that is effective. The result, then, is what would be expected according to the law of Mass Action—the effect of adding aluminium chloride to an aqueous solution of uranyl nitrate causes the same shift of the uranyl bands that would be produced if uranyl chloride were added.

A spectrogram was made of the absorption of uranyl nitrate in water that showed about eight of the uranyl bands, the blue-violet band being about 300 Ångström units in width. The addition of a concentrated solution of calcium nitrate increased the general absorption of the blue-violet band very greatly, so that only the *a*, *b*, and *c* uranyl bands remained. The position and general appearance of these bands did not seem to be changed. Further work of this kind will be done.

To a solution of uranyl chloride in water a concentrated solution of calcium nitrate was added. The uranyl chloride solution showed the *a*, *b*, and *c* bands, and the blue-violet band was about 400 Ångström units in width. The addition of the calcium nitrate caused the blue-violet band to be shifted towards the violet, the shift being greater on the long wave-length edge of the band. The uranyl bands also appear to be shifted towards the violet, although in this particular spectrogram they are so weak that they can hardly be detected. Work of this kind will be done with uranyl sulphate and uranyl nitrate, since the neutral uranyl sulphate bands are quite sharp. The addition of the other salts should also be gradual.

A, plate 16, represents the spectrophotographs of the addition of increasing amounts of calcium nitrate to a uranyl chloride solution in water. The spectrogram shows the gradual shifting of the blue-violet band and the decrease in intensity of the uranyl chloride bands.

B, plate 16, shows a spectrophotograph of the changes produced in a nitric acid solution of uranyl chloride to which increasing amounts of a concentrated solution of aluminium chloride in water are added. The spectrogram shows the very great increase in the amount of the ultra-violet absorption on the addition of the aluminium chloride. The blue-violet band does not appear at all. The uranyl bands are shifted slightly towards the red, and apparently change but slightly in intensity. The change from the first to the second strip is brought about by the addition of three drops of the aluminium chloride solution.

Plate 17 is to show the different effect produced by adding an acid and a neutral salt. *A* represents the absorption of uranyl nitrate in nitric acid to which hydrochloric acid is added, and this plate can be compared directly with *B*, plate 16. *B*, plate 17, on the other hand, shows the effect of the addition of an aqueous solution of aluminium chloride to an aqueous solution of uranyl nitrate.

A, plate 17, shows the increase in the ultra-violet absorption. The great increase is in the intensity of the middle uranyl bands, whereas in the case of the first strip the intensity of the various uranyl bands was much more evenly distributed. A very small amount of hydrochloric acid produced a very great change in the uranyl bands. The addition of aluminium chloride produces a much more gradual change in the position and character of the uranyl bands. It produces a much greater change in the ultra-violet absorption, causing the uranyl bands to shift towards the red and to increase very greatly in intensity.

A, plate 22, shows the effect of the addition of calcium nitrate to an aqueous solution of uranyl nitrate.

CHAPTER V.

EFFECT OF TEMPERATURE ON ABSORPTION SPECTRA.

The purpose of the work on absorption spectra at high temperatures was to obtain some knowledge of the chemical changes that take place at these temperatures, by means of changes produced in the absorption spectra. The cells used have, in the main, been the quartz cell and the two steel cells described in a previous chapter. Some qualitative observations were made with a hand spectroscope on solutions showing water and alcohol bands. The work done with the quartz cell was mainly with acid solutions, and this was done with a view to testing the stability of acid aggregates, as will be explained a little later. Some work was carried out on the change in the relative intensities of various solvate bands with change in temperature. This will also be taken up in detail.

The problem has been found to be a very difficult one, on account of closing the cell tightly, and very largely because of the formation of precipitates upon the windows of the cell.

Some work has been done dealing with the effects of pressure and high temperature upon solutions. W. N. Ipatieff[1] has shown that under a pressure of about 125 atmospheres of hydrogen, anthracene and phenanthrene were reduced, when heated in the presence of nickel oxide, to compounds such as $C_{14}H_{12}$, $C_{14}H_{14}$, $C_{14}H_{20}$, etc. From this work and that of others it has been shown that metals are precipitated from solutions of their salts by hydrogen under pressure. There appears to be a critical temperature for the precipitation of each metal, silver and mercury being precipitated at ordinary temperatures under a pressure of 200 atmospheres from a decinormal solution, while copper and the more electro-positive metals could not be precipitated even when the pressure exceeded 500 atmospheres. At 120° to 130°, however, branched crystals of copper were formed at 100 atmospheres; and at lower temperatures cuprous oxide was formed. Cobalt was precipitated at 180° to 200°, nickel at 200°, lead and bismuth at 240° to 250°, iron at 400° and 420 atmospheres. Ferric oxide was precipitated from an acetate solution at 350° and 230 atmospheres.

Among some of the investigators who have studied the effect of pressure and temperature on the conductivity of solutions are A. Bogojawlensky and G. Tammann in 1898, and F. Körber[2] in 1909. In most cases the resistance decreased as the pressure increased, but in many cases a minimum resistance is reached, after which a further increase in pressure will cause an increase in the resistance. This is true of solutions of potassium chloride at all temperatures between 0° and 100° C. At 0° the minimum resistance is 0.872 of its original value, and is reached at 3000 kg. per sq. cm.; at 100° C. the minimum resistance ratio is 0.998 and this is reached at 900 kg. per sq. cm. Among halogen compounds the largest decrease of resistance is found for hydrogen chloride (17 per cent for $v=100$, $p=3000$ and $t=19°$ C.) and lithium chloride (14 per cent); and then follow potassium chloride (9), sodium chloride (8), potassium bromide (6), sodium bromide (5), potassium iodide (2), and sodium iodide (1).

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[1] Ber. d. chem. Ges., **41**, 966 (1908); **42**, 2078 (1909).

Zeit. phys. Chem., **67**, 212 (1909)

SOLVATES AND THE EFFECT OF CHANGE IN TEMPERATURE ON THE RELATIVE INTENSITY OF SOLVATE BANDS.

The absorption spectra of colored salts, in general, in the visible region are not very characteristic, but the absorption spectra of neodymium, erbium, uranyl, uranous, and a few of the other rare-earth salts show fine characteristic bands, more or less distributed throughout the spectrum. There are, however, even among these spectra, very few cases where the absorption spectra of the same salt in different solvents, or of different salts of the same metal in the same solvent, are very different. There are, however, a few examples of well-defined "solvent bands," and some of these will now be discussed.

The most striking examples of the effect of the solvent on absorption spectra are: those of water and ethyl alcohol upon several of the neodymium salts, water and alcohol upon uranous chloride or uranous bromide, and water and glycerol upon several uranyl and uranous salts. The spectra may well be described as consisting of the "water," the "methyl alcohol," the "glycerol," etc., bands of the particular salt. When the salt is dissolved in a mixture of two of the solvents, both sets of solvate bands appear, and if the solvents are mixed in a certain proportion, both sets of bands may be obtained of approximately the same intensity. The intensity of any set of solvate bands will be proportional to the amount of that solvent present. As the amount of the solvent present is changed, the solvate bands, in general, do not shift their position, but only change in intensity, and this change in intensity seems to be the same for all of the bands characteristic of that solvent. Solvent bands, in this respect, differ from the phosphorescent bands described by Lenard[1] and Klatt.

Just as a characteristic arc or spark spectrum has been regarded as indicating the presence of a certain element, just so a characteristic absorption spectrum will be regarded as evidence for the presence of a compound; and these compounds will be considered as being composed of one or more molecules or ions of the salt ("aggregate") and one or more molecules of the solvent. On account of the definite spectra, we shall speak of the "methyl alcoholate" of uranous chloride, the "hydrate" of neodymium bromide, etc.

Suppose, for instance, that the number of radicles in an aggregate of neodymium salt molecules and ions can vary, then the compound in which absorption takes place might be represented symbolically in the following manner:

$$x\{\overset{\cdot\cdot}{UO_2}\}\,y\{UO_2Cl_2\}\,z\{\bar{Cl}\}\,a\{CH_3OH\}$$

and

$$x'\{\overset{\vdots}{Nd}\}\,y'\{NdCl_3\}\,z'\{\bar{Cl}\}\,a'\{CH_3OH\}$$

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[1] Ann. d. Phys., 31, 612 (1910).

In most cases x, x', z, and z' would probably be small; y and y' may also be small, and if hydrochloric acid or some other chloride is present, it might be possible to have systems of the following composition:

$$x_1\left\{\overset{++}{UO_2}\right\}x_2\left\{\overset{+}{H}\text{ or }\overset{++}{Ca}\ \ldots\right\}y_1\left\{UO_2Cl_2\right\}y_2\left\{HCl,CaCl_2\ \ldots\right\}z\left\{\overset{-}{Cl}\right\}a\left\{CH_3OH\right\}$$

$$x_1'\left\{\overset{+++}{Nd}\right\}x_2'\left\{\overset{+}{H},\overset{++}{Ca}\ \ldots\right\}y_1'\left\{NdCl_3\right\}y_2'\left\{HCl,CaCl_2\ \ldots\right\}z'\left\{\overset{-}{Cl}\right\}a'\left\{CH_3OH\right\}$$

The absorption may be due to some condition, possibly one of internal ionization of the aggregate, and as long as the number of aggregates remains constant, Beer's law will hold. Free ions may split off from the aggregate without the character of the absorption being greatly changed. It might be that if the aggregates were completely broken up into their constituent ions and molecules no characteristic absorption would be shown.

In this case, a and a' may either be considered as being constant, or as being so large that the atmosphere of the solvate around the absorber is so extensive that it is immaterial whether the outer solvent molecules are present or not. On account of the fact that solvent bands coexist, and do not shift into each other as the proportion of the solvents is changed, it will be assumed that at least the inner and effective solvent molecules are all of one kind in any "spectral" compound.

As to the numerical value of the y's the absorption spectra of course do not furnish evidence. The phenomena of the constancy of the wave-length of the uranyl sulphate and uranyl nitrate bands, with great dilution of these salts, leads to the conclusion that in this case at least the value of y is greater than unity. Freezing-point, boiling-point, conductivity, and osmotic pressure measurements should aid in determining the values of x, y, and z in the above equations.

The existence of complex aggregates of the above kind is quite rare in inorganic chemistry, although cases have been known. Our own work on the reduction and oxidization of certain uranium salt and acid aggregates has shown that these different aggregates have very different chemical properties. Some cases of a series of a similar set of compounds might be cited, *e.g.*, the cobaltamines. A large number of cobaltamines are known, and these have been divided into six series.

The diamine series $[Co(NH_3)_2]X_4M$. In this series $X=NO_2$ and M is one atomic proportion of a monovalent metal, or the equivalent quantity of a divalent metal. These salts are prepared by the action of alkaline nitrites on cobaltous salts in the presence of a large amount of ammonium chloride or nitrate. The salts are yellow or brown crystalline solids, and are not very soluble in water.

The triamine series $[Co(NH_3)_3]X_3$. X may be Cl, NO_3, NO_2, $\frac{1}{2}SO_4$, etc.

The tetramine series, including,

Praseo salts $[R_2Co(NH_3)_4]X$. $X=Cl$.
Croceo salts $[(NO_2)_2Co(NH_3)_4]X$.
Purpureo salts $[RCo(NH_3)_4,H_2O]X_2$.
Roseo salts $[Co(NH_3)_4(H_2O)_2]X_3$.
Fuseo salts $[Co(NH_3)_4]OH\,.\,X_2$.

For the methods of preparation see O. Dammer's Handbuch der anorganischen Chemie, vol. 3.

The pentamine purpureo salts $[RCo(NH_3)_5]X_2$, where X may be Cl, Br, NO_3, NO_2, $\frac{1}{2}SO_4$, etc. The pentamine nitrito salts are known as the xanthocobalt salts, and have the general formula $[NO_2Co(NH_3)_5]X_2$. The pentamine roseo salts can be obtained by the action of concentrated acids in the cold on oxidized solutions of cobaltous salts. They are of a reddish color. On heating with concentrated acids they become purpureo salts.

The hexamine or luteo series has the composition $[Co(NH_3)_6]X_3$. These salts form yellow or bronze-colored crystals which decompose on boiling. The above examples are cited because the cobalt salts give an absorption band spectrum in some cases similar to the uranyl bands. It is very probable that uranium, neodymium, erbium, etc., give rise to much more complex compounds than even cobalt.

It will be assumed that the absorption bands are due to compounds that represent the average condition of the given dissolved salt. It may be that only a few of the particles of the absorbing salt may be active at any one instant. For instance, Becquerel[1] considers that only a very small number of the neodymium atoms are taking part in the absorption of light at any moment. It may be that the absorption only takes place when the compound is in a special condition. For example, in the case of the uranyl salts we may think of the absorption as being due to the valency electrons in the UO_2 group. The absorption may take place when one of these electrons leaves the uranium or oxygen atoms, or when it returns. Whatever the mechanism may be, it will be assumed that the frequency of the absorber is determined by the nature of the compound in which it is located, and that this compound is typical of the average of all the possible compounds in the solution. Accordingly, if the "methyl alcohol" and "water" bands of uranous bromide dissolved in methyl alcohol and water are of approximately the same intensity, it follows that there are equal amounts of the uranous bromide existing as the "methyl alcoholate" and as the "hydrate."

In the case of neodymium chloride or neodymium bromide Jones and Anderson[2] have shown that the "water" and "alcohol" bands are of about equal intensity when the solution consists of 8 per cent of water and 92 per cent of alcohol. In the case of uranous bromide or uranous chloride in water and methyl alcohol, it is found that the "water" and "methyl alcohol" bands are of about equal intensity when there are approximately 2 parts of water to 3 parts of methyl alcohol in the solution. In the case of the neodymium salts it would seem that the "water" bands are the more "persistent." The less "persistence" of the "hydrate" of uranous chloride or uranous bromide may be due to the presence of the zinc salts formed during the reduction of the uranyl salts. It is found that the presence of free hydrochloric acid in a solution containing the "hydrate" and "methyl alcoholate" of uranous chloride causes the "water" bands to decrease in intensity with reference to the "methyl alcohol" bands. The action of any chloride would probably be the same. In the case of neutral salts of neodymium and uranium the "water" bands are usually more persistent than the "glycerol" bands, and these in turn are more persistent than the "alcohol" bands.

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[1] Becquerel. Le Radium, Sept. (1907).

[2] Phys. Rev., **26**, 520 (1908).

In the case of neodymium chloride in a mixture of 92 per cent alcohol and 8 per cent water it has been found[1] that Beer's law does not hold, the "water" and "alcohol" bands being of about equal intensity for a 0.5 normal solution, while for a 0.05 normal solution the "water" bands are much stronger than the "alcohol" bands. Whether the "water" bands in general show such a "persistence" is being investigated.

On the other hand, it has been found that the "alcoholates" are much more "persistent" than the "hydrates" at the higher temperatures. This is especially pronounced in the case of the "water" and "alcohol" bands of uranous chloride and uranous bromide. If the two sets of bands are of equal intensity at ordinary temperatures, at 80° C. the "water" bands have practically disappeared. This observation can easily be verified with a small pocket spectroscope.

Several very characteristic spectra have been obtained for neodymium salts dissolved in isomeric alcohols. The bands of neodymium chloride in isobutyl alcohol are of considerably greater wave-length than the corresponding bands of neodymium chloride in butyl alcohol; whereas the "propyl alcohol" bands are displaced to the red with reference to the "isopropyl alcohol" bands. The "butyl" and "isobutyl" bands of neodymium nitrate are very much alike, while the "propyl" bands are displaced to the red as compared with the "isopropyl" bands, being in the same direction as for the chloride.

Neodymium Chloride in Water and Ethyl Alcohol.

A, plate 52, represents the absorption of a 0.3 normal solution of neodymium chloride in water and ethyl alcohol. The temperature range is from 40° to 80° C. The original film shows that at the higher temperatures the water band λ 4271 almost disappears, while the alcohol band becomes stronger. The ϵ group shows the same thing in a general way, in that the total absorption, especially on the violet side of the band, is much less at the highest temperature than at the lowest temperature.

B, plate 52, shows the same effect for a more dilute solution. The finer water bands of the α, δ, and ϵ groups are shown by the original film practically to disappear at the higher temperatures, while the alcohol bands become more intense.

Neodymium Bromide in Water and Methyl Alcohol.

C, plate 53, represents the absorption of neodymium bromide in water and methyl alcohol, 0.2 normal and 1.0 cm. length of cell. The variations in temperature were from 30° to 80° C.

In the lower strip the alcohol band at about λ 4285 hardly appears at all, while the water band at λ 4271 is quite strong. At 80° the water band is still quite strong, and the alcohol band is possibly a third as strong as the water band.

Neodymium Chloride, Bromide, and Nitrate in Water.

B, plate 55, strip 1, shows the absorption of a 2.05 normal solution of neodymium chloride in water at 20°; strip 2 is the same at 50°, and strip 3 is the same at 75°.

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[1] Phys. Zeit., **11**, 671 (1910), **12**, 269, (1911).

A, plate 55, represents the absorption of a 1.66 normal aqueous solution of neodymium bromide at 20°, 40°, 60°, 80°, and 93°, the highest temperature being that represented by the upper strip.

B, plate 55, strip 4, represents the absorption spectrum of a 2.05 normal aqueous solution of neodymium nitrate at 20°, strip 5 at 75°, and strip 6 at 95°.

These spectrograms show the very great increase in the absorption of the short wave-lengths as the temperature reaches about 90°. The spectrograms show the widening of the individual neodymium bands. There is a slight shift towards the red with rise in temperature, but this is very small. The absorption spectra of the three solutions are practically the same, that of the chloride and bromide being nearly identical, while that of the nitrate differs a little in some of the minute details of the individual bands.

NEODYMIUM CHLORIDE IN METHYL ALCOHOL.

Plate 54, *A*, represents the absorption of a 0.1 normal solution of neodymium chloride in methyl alcohol, 10 cm. depth of cell. This spectrogram shows the methyl alcohol bands quite sharply. A weak band appears on the first strip at λ 4015, and at λ 4200. λ 4285 is quite strong and only about 10 Ångström units wide. A weak and quite narrow band appears at λ 4270. The band λ 4270 is rather hazy; λ 4450 is about 50 Ångström units in width and is very diffuse, its red side not being as diffuse as the violet side. λ 4620 is very weak; λ 4700, λ 4770, and λ 4820 all have about the same intensity and width, the first two being accompanied by very weak bands on their violet sides at λ 4680 and λ 4750. λ 5040 is very weak and broad; λ 5120 is about 20 Ångström units wide and is very strong. λ 5175 is very similar to λ 5120, except that it is only about one-half as intense. λ 5215, λ 5250, and λ 5290 are all very intense and are quite sharp, the middle band being about 20 Ångström units in width, while the other two are only about 10 Ångström units wide. There is a wide absorption band from λ 5710 to λ 5940, with the sharper edge on the violet side. The red band at λ 6850 appears to be quite strong and about 20 Ångström units in width.

The other strips represent the same solution at different temperatures, these being 15°, 26°, 40°, 55°, 78°, and 85°, starting with the lowest strip.

With rise in temperature the bands all become somewhat more intense and wider. The general absorption over the whole spectrum region increases, especially at the higher temperatures, and begins to encroach quite rapidly in the violet and red regions. This violet absorption is probably a general absorption, but the encroaching on the red side is probably due to the increase in the intensity of the group of red bands.

In the upper strip transmission extends from about λ 4200 to λ 6100. A very weak band appears at λ 4200 and a very weak one at λ 4305. The bands in the blue and green have changed but little. Absorption is pretty complete from λ 5100 to λ 5190, λ 5210 to λ 4350, and from λ 5690 to λ 5990. Weak bands appear at λ 6230, λ 6280, and λ 6750. If any of the bands showed any shift it was too small to measure. The band at 15°, extending from λ 5710 to λ 5940, widens approximately 20 units on its violet side and 50 units on its red side. It is probably more or less general that wide absorption bands usually broaden unsymmetrically towards the red, especially when this side is the more diffuse.

A, plate 53, represents the absorption of a methyl alcohol solution 0.2 normal and with 1.0 cm. depth of cell. The temperatures are 25°, 40°, 55°, and 70°. The only important change due to temperature is that at 70°, the intense absorption near the center of the ϵ group of bands having practically disappeared.

Neodymium Bromide in Methyl Alcohol.

B, plate 54, represents the absorption spectrum of a 0.1 normal solution of neodymium bromide in methyl alcohol. The length of cell was 10 cm. The temperatures were 25°, 35°, 44°, 60°, 82°, 100°, and 120° C., beginning with the lowest strip. At the highest temperature a slight precipitate was formed, but still some light was transmitted. The neodymium solutions all become much more deeply colored at the higher temperatures, and this can easily be shown by heating such a solution in an ordinary test tube.

The absorption spectrum of neodymium bromide in methyl alcohol is quite different, as far as minute detail goes, from that of the chloride. In general, the bands of the chloride are from 5 to 15 Ångström units farther towards the red than the bromide bands.

For the lowest strip, very weak and diffuse bands appear at about λ 4000, λ 4180, λ 4600, λ 4900, λ 5040, λ 5320, λ 6230, λ 6260, λ 6730, and λ 6790. The β group of the bromide is very different from that of the chloride. It consists of a very sharp, narrow (3 units) band at λ 4265, a very sharp and less intense band at λ 4275, a hazy band at about λ 4280 which more or less overlaps λ 4275, and at higher temperatures λ 4275 can not be noticed at all. A very weak band appears at λ 4300 and a broader band at λ 4325, being about 20 Ångström units in width.

The γ group of the chloride is also quite different from that of the bromide, which has four bands of almost equal intensity at λλ 4690, 4745, 4765, and 4815. Weak bands appear at λ 4670, λ 4700, and λ 4725. The δ group consists of a rather narrow band at λ 5090 and a very strong band at about λ 5115; a lot of narrow and intense bands at λ 5200, λ 5220, λ 5235; λ 5250 and λ 5275 practically merge into a single band. The ϵ group consists of a single wide band extending from λ 5700 to λ 5880.

As the temperature is raised the violet absorption increases quite rapidly, and the δ and ϵ groups of bands become wider and stronger. The latter band widens very greatly towards the red. All the bands become very much more diffuse. This is particularly true of the β group, since at 120° only two very hazy, indistinct bands appear, while at 25° some of the bands in this group were almost as fine as spark lines.

No measurable shift of the bands towards the red could be observed.

That the absorption spectra of the chloride and the bromide in methyl alcohol should be so different was quite unsuspected, since these two salts have almost identically the same absorption spectra in aqueous solution.

Neodymium Nitrate in Isobutyl Alcohol.

The absorption spectrum of a solution of neodymium nitrate in isobutyl alcohol was photographed at 20°, 45°, 75°, 95°, 110°, and 120° C. The concentration was 0.05 normal and the depth of cell 10 cm. The first strip of this spectrogram is described under the chapter on the mapping of spectra.

The general result of rise in temperature is to cause a large increase in the general absorption in the ultra-violet. This is especially strong at 120°, where the general absorption is complete to about λ 4100, and extends as a partial absorption to beyond λ 5000. The neodymium bands are considerably widened by rise in temperature, and are shifted in many cases some 15 or 20 Ångström units towards the red (120° compared with 20°).

Some of the more pronounced changes may be noted if the following wave-lengths are compared with those described under the chapter on mapping of spectra. At 120° a weak band appears at λ 4260. It is about 10 Ångström units wide. The other bands of the β group are at λ 4295, λ 4305, λ 4325, and λ 4360. The lines of the γ group are at λ 4725, λ 4775, and λ 4850. The δ group consists of the wide band at λ 5140 and the double band at λ 5250 and λ 5275. The ε group runs from λ 5720 to λ 5960 as a single band.

Neodymium Nitrate in Acetone.

A spectrogram was made of the absorption spectrum of a solution of neodymium nitrate in acetone, in the long cell, at 16°, 40°, 70°, 100°, and 180°. The solution became opaque at about 110°, and afterwards quite transparent at about 160°.

The effect of the rise in temperature was to cause a slight shift of the neodymium bands to the red, but as these bands were so very broad and hazy, no measurements could be made. The strip taken at 180° shows a very great absorption in all regions except the yellow and red, and the absorption in the red is, indeed, almost complete. There is no indication of any neodymium bands at all, so that it seems that practically all the neodymium nitrate had been precipitated.

Erbium Chloride in Water.

A, plate 60, represents the spectrum of an aqueous solution of erbium chloride at 20°, 30°, 85°, and 115° C.

The effect of rise in temperature on the individual erbium bands is very small, their diffuseness being hardly increased with rise in temperature. The increase in the general absorption throughout the region of smaller wave-lengths is enormous, resulting in the solution being practically opaque at the higher temperatures.

Strip 1 shows the following bands, the wave-lengths being only approximate: a band from λ 3430 to λ 3520; a strong band at λ 3540 which is about 10 Ångström units wide; weak bands at λ 3555, λ 3570, and λ 3595; the previous band is the beginning of a region of absorption that extends to λ 3660; a group of three bands that practically merge into a single band running from λ 3750 to λ 3790; weak bands at λ 3800 and λ 3840; diffuse bands at λ 3870; strong λ 3900, λ 3950 weak, λ 4000 weak; λ 4045 sharp and narrow (10 units); λ 3070 sharp and narrow; λ 4100 very weak; λλ 4155, 4165, 4185, 4215—these bands are much alike, the first being the most intense; λ 4270 is wide and very weak; λ 4430 diffuse; λ 4450 very weak; λ 4480 weak; λ 4500 strong; λ 4530 is apparently covered by a diffuse band on its red side; λ 4685 weak; λ 4750 and λ 4800 wide and weak; λ 4855 narrow; λ 4880 intense; λ 4930 probably double; λ 5200; λ 5225; λ 5245 intense; λ 5290 weak; λ 5380; λ 5390 weak; λ 5435; λ 5455; λ 5520 weak; group at λ 5770 very weak; λ 6440, λ 6460, λ 6530, λ 6560 strong. λ 6600 and λ 6710 all very diffuse and having a very "washed-out" appearance.

URANYL CHLORIDE IN ACETONE.

A spectrogram was made of the absorption spectrum of a solution of uranyl chloride at 22°, 40°, 60°, 170°, 185°, and 195°. At about 70° a precipitate was formed, but the solution became transparent again at 160°.

At 22° six of the uranyl bands appear, some being clearly double, as is characteristic of the acetone bands. At 40° only two bands appear, the general absorption throughout the violet and blue regions of the spectrum being so great. At 60° no uranyl bands appear at all, the short wave-length absorption extending to about λ 5500. After the formation of the precipitate there is quite a strong transmission in the violet and about five uranyl bands appear. The uranyl bands are weaker and considerably narrower at the higher temperatures. Above 60° the bands appear to be single. From 170° to 195° the uranyl bands rapidly decrease in intensity, and at 195° they are so weak that one can not be certain that they can be seen at all. At the same time the general absorption in the violet increases, but not to any great extent.

URANYL NITRATE IN PROPYL ALCOHOL.

B, plate 64, represents the absorption of a 0.005 normal solution of uranyl nitrate in propyl alcohol, the depth of cell being 10 cm. The temperatures, starting at the lowest strip, are 20°, 40°, 65°, 85°, 105°, 115°, 130°, and 145°. The sixth and seventh strips show a very weak transmission on the violet side of the blue-violet uranyl band. At 145° this has become a broad region of transmission. This spectrogram shows the enormous extension of the general absorption as the temperature rises.

The first strip shows the uranyl bands λ 4085, λ 4200, λ 4330, and λ 4470.

URANYL CHLORIDE AND NITRATE IN ISOBUTYL ALCOHOL.

A, plate 62, represents the absorption of a 0.076 normal solution of uranyl chloride in isobutyl alcohol at 20°, 60°, 85°, and 115° C.

B, plate 62, represents the absorption of uranyl nitrate of 0.033 normal concentration in isobutyl alcohol, the temperatures being 20°, 50°, 80°, 100°, and 105° C.

In the case of the chloride solution the uranyl bands are quite strong and fairly sharp. The two bands that show are at λ 4570 and λ 4730. In the case of the nitrate solution only a single band at about λ 4630 appears. This band is very diffuse and weak. For aqueous solutions, as will be remembered, the reverse is the case, the chloride bands being very weak and diffuse and the nitrate bands being quite strong and narrow.

URANYL CHLORIDE AND NITRATE IN METHYL ESTER.

B, plate 66, represents 0.005 normal solution of uranyl nitrate in methyl ester at 20°, 50°, 75°, and 100° C. The spectrogram shows that the uranyl bands are quite strong and clear. As the temperature rises the general violet absorption increases, and the uranyl bands are slightly shifted towards the red. The approximate wave-lengths of some of the bands are λλ 3900, 4020, 4130, 4250, 4380, 4520, 4670, and about 4820, this last band being very weak.

B, plate 63, shows uranyl and calcium chlorides in methyl ester (first three strips), and uranyl and calcium chlorides in methyl alcohol (last three strips). The temperatures are 20°, 45°, 85°, 20°, 50°, and 95° C. The methyl ester at 20° showed very strong bands at λλ 4600, 4760, and 4930.

It was thought that by adding a large amount of a salt like calcium chloride to solutions of uranyl chloride in different solvents the absorption spectra of the resultant solutions would be more alike. The spectrogram shows that this is not the case, since it will be seen in the lower strips that the uranyl bands are very strong and quite sharp, whereas in the case of the methyl alcohol solution the bands are very wide and very weak. Their wave-lengths are also considerably greater than those of the bands in the ester solution. These spectrograms show that although double salt aggregates may be formed, the solvent part of the aggregate still plays a very important rôle in influencing the wave-lengths of the absorption bands.

The effect of the addition of calcium chloride to the ester solution was not tested by regular steps, but for the pure uranyl chloride solution the *a* band appears as a double band with the components at about λ 4930 and λ 4965. These bands practically merge into one another, and it is rather difficult to see that the band is really double. Apparently the effect of the addition of calcium chloride is to cause the component λ 4965 to disappear, and, at the same time, the other component widens. The methyl ester solutions offer a promising field for studying the spectrophotography of chemical reactions and also for the effect of dilution.

A, plate 64, represents the absorption of 0.005 normal solution of uranyl chloride in methyl ester, the depth of cell being 10 cm. The temperatures, starting with the lowest strip, are 20°, 45°, 70°, 90°, 110°, 135°, and 140° C.

At 20° the following uranyl bands appear: λ 3930 fine and weak; λ 4050 quite narrow; λ 4170, λ 4300, λ 4450, λ 4630, and λ 4800 probably the *b* band. At 140° C. only the *b*, *c*, and *d* bands appear at λλ 4480, 4650, and 4820. At the highest temperature the transparency of the solution in the violet has apparently increased. The character of the uranyl bands is but slightly affected by the above temperature changes.

Uranous Chloride in Water and Methyl Alcohol.

Strip 5, *A*, plate 67, represents the absorption of uranous chloride in a mixture of water and methyl alcohol, in such proportions that the water and alcohol bands were of about equal intensity at 10° C. Strip 6 represents the same solution at about 70° C.

These strips show that at the higher temperature the uranous water bands have almost disappeared. The uranyl bands have also become very much weaker, and the uranous alcohol bands slightly weaker. No appreciable shifting of the bands is to be noticed.

Uranous Chloride in Acetone.

A spectrogram of the absorption spectrum of uranous chloride in acetone was taken at 20°, 40°, 65°, 80°, 95°, and 105°.

At about 60° a precipitate was formed, and above this temperature the red absorption band hardly appears at all. The uranous bands in the green and yellow seem to be considerably stronger after the formation of the precipitate.

THE EXISTENCE OF AGGREGATES AND THEIR PROPERTIES, AND THE EFFECT OF RISE IN TEMPERATURE ON THE AGGREGATES.

The presence of free acid[1] or of other salts has been found, in many cases, to modify very considerably the uranyl, uranous, and neodymium bands of a given salt in solution. Up to the present, work of this kind has been practically restricted to aqueous solutions, although similar changes take place in other solvents. One of the most pronounced cases is that of the uranyl nitrate and the uranyl chloride bands. Most of the nitrate bands have shorter wavelengths than the chloride bands. As increasing amounts of hydrochloric acid are added to an aqueous solution of uranyl nitrate, the nitrate bands are found to shift gradually into the position of the chloride bands. Furthermore, the addition of nitric acid to an aqueous solution of uranyl nitrate causes most of the uranyl bands to shift towards the violet, whereas the addition of hydrochloric acid to an aqueous solution of uranyl chloride causes most of the bands to shift towards the red. These changes are quite different from those that take place when the solvent is changed; and if it is supposed that a characteristic absorption spectrum corresponds to a more or less stable compound, then these changes indicate a series of compounds which will be referred to as aggregates. We would have, then, nitric acid aggregates of uranyl nitrate, or hydrochloric acid aggregates of neodymium chloride.

Whether there is an actual change in the frequency of vibration for a series of uranyl or uranous aggregates, or whether there is simply a relative change in the intensity of a number of finer bands which blend into the rather broad and diffuse bands that are photographed, can not be decided at present. In the case of neodymium salts[2] the various spectrophotographs indicate the latter effect. It is unlikely that the case can be settled very easily for uranyl and uranous salts, since the greatest shifts take place in the absorption of aqueous solutions, and these can not be studied at very low temperatures. Subsequently, it will be assumed that a spectrogram of a chemical reaction showing a gradual shifting of bands indicates the presence of a series of closely related aggregates existing in the solution.

The mixture of varying proportions of two neutral salts in a solution may result in a gradual change from the bands of one salt into the bands of the other salt (mixtures of uranyl nitrate and uranyl chloride in water). On the other hand, there are cases in which each salt seems to have its own definite spectrum. In this case there will be no shifting of the bands but only a change in intensity, and we may assume that, in this case, there are no double salts formed. In the former case, however, it seems probable that there are aggregates formed which contain one or more molecules of each salt.

The addition of salts[3] containing the same cation as the corresponding uranyl or uranous salt, has an effect similar to that of the addition of free acid, and may be considered as indicating the presence of aggregates. In the case of uranyl chloride the effect seems to be due largely to the chlorine present.

Acid aggregates of uranous salts are found to be much more stable than the neutral aggregates. Uranous nitrate, for example, is very unstable, but uranous chloride dissolved in concentrated nitric acid will stand for hours before it is oxidized to the uranyl condition. Most of the neutral uranous salts are precipitated when heated to 80° or 90° C.; but if some free acid, or if in the case of uranous chloride other chlorides are present, the uranous salts are stable at these higher temperatures.

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[1] Phys. Zeit., 11, 668 (1910), 12, 269 (1911).

[2] *Ibid.*, 11, 671 (1910), 12, 269 (1911).

[3] Publication No. 130, Carnegie Institution of Washington, p. 91.

It might be expected that if the effect of rise in temperature is to break up aggregates, then in the case of concentrated acid solutions of the uranyl salts the shift towards the red should be very great for a concentrated nitric acid solution of uranyl nitrate; while in the case of a hydrochloric acid solution of uranyl chloride, or of a sulphuric acid solution of uranyl sulphate, the shift should be in the opposite direction. On the other hand, if the shift caused by change in temperature is due to some other cause and the aggregates are not broken up, no effect of this kind would be expected.

In a solution of uranous sulphate in sulphuric acid the uranyl bands are slightly shifted to the red as the temperature is raised from 10° to 90°, while the uranous bands are slightly shifted to the violet. The shift of the neutral uranyl sulphate bands to the red is greater than that of the acid sulphate bands. The shift of the uranyl nitrate bands in nitric acid is about 15 Ångström units. All bands are shifted about the same amount.

NEODYMIUM SALTS IN ACID SOLUTIONS.

Plate 59, *A*. This spectrogram shows the effect of hydrochloric acid, sodium chlorate, and temperature on the neodymium chloride bands. Strip 1 is the absorption of neodymium chloride in water at about 10°, strip 2 the same at about 90°. Strip 3 represents the absorption of the same amount of neodymium chloride in concentrated hydrochloric acid at 10°, strip 4 the same at 90°. Strip 5 represents the absorption at 10° of neodymium chloride in methyl alcohol, and strip 6 the same containing sodium chlorate.

Plate 59, *B*. This spectrogram shows the absorption of a 0.02 normal solution of neodymium acetate at 10° in strip 1 and at about 90° in strip 2. Strip 3 represents the absorption of a small amount of neodymium chloride added to acetic acid so as to fill the quartz cell at 10°, and strip 4 the same at 90°. Strip 5 represents the absorption of neodymium acetate in acetic acid at 10°, and strip 6 the same at about 90°. Strip 7 represents the absorption of a solution in methyl acetate and acetic acid at 10°, and strip 8 the same at 90°.

The first two strips in *A* show that the effect of rise in temperature on an aqueous solution of the chloride is to cause a very slight shift of the bands towards the red, and to give them a much more diffuse and washed-out appearance. The hydrochloric acid solution of neodymium chloride shown in strips 3 and 4 is but very slightly changed by rise in temperature, and there is no indication that the spectrum becomes more closely like that of the neutral aqueous solution. The shift to the red is very small. It can easily be noticed for the bands of the ϵ group. At 10° the long wave-length bands of the δ group are very much like the two bands of the neutral aqueous solution. At 90° these bands have both become very diffuse, blending into a single band, and the whole center of the band is greatly shifted towards the red. This is the greatest temperature change in the whole spectrum. The presence of sodium perchlorate in a methyl alcohol solution of neodymium chloride causes the neodymium bands to be shifted very slightly towards the violet.

A neutral acetate solution in water, as shown in strips 1 and 2 of *B*, is affected like the neutral chloride solution, in that at the higher temperature the bands have a much more diffuse washed-out appearance. This is especially true of the α group, which appear very weak at 90°. Very little shifting of the bands towards the red takes place. Strips 4 and 5 show about the same effect and the same very great decrease in the intensity of the α group at the higher temperature. In the next two strips the α group remain of about the same intensity at the two temperatures. There is less increase in the diffuseness of the acetate bands in acetic acid than in the case of a neutral acetate solution.

Plate 56, *A*. This spectrogram represents the absorption of neodymium chloride in acetone at 10° (strip 1) and at 70° (strip 2); neodymium chloride in ether at 10° (strip 3; a precipitate is formed at higher temperatures); neodymium chloride in ethyl alcohol 0.02 normal at 10° (strip 4) and about 70° (strip 5); neodymium chloride in ethyl alcohol to which hydrochloric acid gas has been added at 10° (strip 6) and at about 70° (strip 7).

Plate 56, *B*. This spectrogram represents the absorption of neodymium nitrate in nitric acid at 10° (strip 1) and at about 50° (strip 2; if heated to much higher temperatures nitrous oxide is formed); of neodymium chloride in methyl alcohol and 8 per cent of water at 10° (strip 3) and at about 70° (strip 4); neodymium nitrate in acetone and 8 per cent water at 10° (strip 5) and at about 60° (strip 6); neodymium chloride in 60 per cent ethyl alcohol and 40 per cent water at 10° (strip 7); and neodymium chloride in 40 per cent water and 60 per cent glycerol at 10° (strip 8).

The acetone solution of neodymium chloride shows very little if any change with rise in temperature. The ethyl alcohol solution shows a small increase in the diffuseness, and a very great shift of the intensity of the band groups with rise in temperature. When hydrochloric acid is present there is very little change of this kind. The new and very strong bands appear at about λ 3590 and λ 3750, the latter band being about 50 Ångström units wide.

The nitric acid solution of neodymium nitrate shows very little change in the absorption spectrum with rise in temperature. The bands become somewhat more diffuse and decrease in intensity. The red bands do not show in the strips. Strips 3 and 4 show the very considerable increase of the alcohol bands over the water bands. The α, β, and δ fine water bands have practically disappeared at the higher temperature.

URANOUS SULPHATE IN SULPHURIC ACID.

Plate 67, *A*. The absorption of uranous sulphate in sulphuric acid at 10° is represented in strip 1, and at about 90° in strip 2. The absorption of the neutral uranous sulphate in water at 10° is shown in strip 3, and at about 90° in strip 4. The absorption of uranous chloride in water and in methyl alcohol at 10° is shown in strip 5, and at about 70° in strip 6. The uranyl bands of the sulphuric acid solution are shifted towards the red with rise in temperature, whereas the uranous bands seem to be shifted slightly towards the violet.

Uranyl Nitrate in Nitric Acid, Uranyl Chloride in Hydrochloric Acid, and Uranyl Sulphate in Sulphuric Acid.

Plate 67, *B*. The absorption of uranyl nitrate in nitric acid at 10° is represented in strip 1, and at about 70° in strip 2; of uranyl chloride in hydrochloric acid at 10° in strip 3, and at about 80° in strip 4; of uranyl sulphate in water at 10° in strip 5, and at about 80° in strip 6; of uranyl sulphate in sulphuric acid at 10° in strip 7, and at about 70° in strip 8.

Every one of the uranyl nitrate bands, due to the rise in temperature, seems to be shifted about 10 Ångström units towards the red, the uranyl chloride bands in hydrochloric acid being shifted about 15 Ångström units.

In the case of uranyl sulphate, only the uranyl bands in the region of the blue-violet band were greatly shifted towards the red with rise in temperature. The shift seemed to be considerably greater for the neutral than for the acid solution.

According to the aggregate theory we might expect that if the uranyl nitric acid aggregates break down at the higher temperatures, the uranyl bands would be very greatly shifted towards the red on account of less nitric acid molecules affecting the uranyl vibrations. But this does not seem to be the case to any very great extent, since here the shift to the red is not any greater than for the other uranyl bands, and seems to be about the same for each one of the bands. It may be considered that the hydrate is more simple, however, and that this allows more of the nitric acid molecules to come within the range of the absorbing centers, and this might in a way counteract the effect of any decomposition of aggregates. Whether the effect of an increase in the number of molecular collisions brings a greater number of nitric acid molecules within the effective range of the absorbing centers, and has an effect on the frequency, can not be decided from the spectrograms.

The very considerable shift of each one of the uranyl chloride bands of the hydrochloric acid solution towards the red with rise in temperature probably indicates that there is very little decomposition of the uranyl acid chloride aggregates.

Since apparently only the *e*, *f*, *g*, and *h* uranyl sulphate bands are greatly shifted towards the red, we might assume that there is a slight decomposition of the uranyl sulphate aggregates, and this counteracts what we might call the normal temperature shift.

In the above strips temperature has very little effect on the uranyl bands, except a shifting of their wave-lengths towards the red.

CHAPTER VI.

SUMMARY AND GENERAL DISCUSSION OF THE MOST IMPORTANT RESULTS.

MAPPING OF SPECTRA.

The first problem to be solved in a study of absorption spectra is the recording of the spectra themselves. The method employed in this series of investigations is that of photographing the absorption spectrum of a solution placed in a beam of light having a continuous spectrum. Such a photograph may be called a spectrogram or a map of the given absorption spectrum.

The study of the spectrograms of colored solutions shows that this color is due to a selective absorption of the solution in some part of the spectrum, and the extent of this selective absorption may be over regions of the spectrum hundreds of Ångström units in width, or over regions only a fraction of an Ångström unit wide—a width that is not much greater than that of a spark or arc line. In fact, bands of almost all widths and degrees of diffuseness are found in addition to the absorption, which is one-sided. If the region of one-sided absorption lies in the red, it is probable that it has another edge in the infra-red. Practically all solutions show an encroaching general absorption in the ultra-violet as the amount of the solution in the path of the light is increased or as the temperature is raised.

The plates and the description of these plates in Publications Nos. 60, 110, 130, and the present monograph of the Carnegie Institution of Washington give a pretty thorough representation of the details of the absorption spectra of most of the typical solutions of the colored inorganic salts.

It can be said, in general, that the absorption spectra of the various salts of the same element are very much alike; indeed, so much alike that it is only when considerable dispersion is used that any differences can be noted. It can also be said that the absorption spectra of the same salt in various solvents are very similar. For these reasons we are justified in assuming that the color of solutions of colored salts dissolved in colorless solvents is due primarily to the metal or metallic radicle of the colored salt. The various spectra that are characteristic of a given kind of salts, say the uranous salts, will, therefore, be called the uranous spectra.

In the mapping of the absorption spectra of solutions of increasing concentration or of increasing depth, it is always found that the absorption bands widen and become more intense as the amount of salt in the path of the beam of light is increased. It can also be stated, as an approximately general law, that the more diffuse a band is the greater will be the widening under these conditions. Examples of this kind are shown by the uranous bands, which may widen from fifty or a hundred Ångström units to a width of thousands of Ångström units. The widening of single, very sharp bands with increasing amounts of the salt in the path of the light is invariably small. As an example we can take the λ 4271 neodymium chloride water band.

When characteristic absorption spectra of salts of the rare earths, of cobalt, chromium, etc., are studied with the use of a high-dispersion spectroscope, it is found that the finer absorption bands are different for the same salt in different solvents, and for different salts in the same solvent. This difference may be a difference in the number of the bands present, a difference in the intensity and width of the bands, or a difference in wave-length.

It can be said, in general, that the absolute differences of intensity, diffuseness, and wave-length, under these conditions, is greater for the larger and the more intense bands. Unfortunately the very large bands are usually so situated in the spectrum that only small changes in the amount of salt can be made before the band becomes one-sided on account of the comparatively small region of the spectrum that can be investigated by photographic methods. But it can be said that the uranous bands show greater changes with change of salt or solvent than the uranyl bands; that the uranyl bands show greater changes than the neodymium bands, and these in turn seem to show much greater changes than the dysprosium and samarium bands; and these, in turn, probably greater changes than the erbium bands.

When we consider the minute structure of the bands and groups of bands under high dispersion we find very great differences, especially in the case of neodymium. The different salts of neodymium in the same solvent, especially in some of the organic solvents, give entirely different absorption spectra. The same is true of the same salt in different solvents. Isomeric solvents very often show characteristic spectra. The absorption bands of neodymium have been divided into groups α, β, γ, δ, ϵ, etc. When there is a large amount of salt in the path of the beam of light, each group usually forms a single broad band. It is found that the relative intensities and characteristics of these groups is very much the same for different salts in different solvents. The minute structure of the bands in the same group is usually more widely different than the absorption spectra of dysprosium and samarium; so that it is quite probable that if the region of spectrum that we could study were wide enough to include one of these groups and sufficient dispersion was at hand, we would consider that we were dealing with different elements whenever the salt and the solvent were changed.

The spectrograms and the descriptions in detail give a large number of examples illustrating the above. Very much more work of this kind remains to be done with solutions like those of neodymium at low temperatures, using very high dispersion.

From the above description of absorption spectra it follows at once that any law such as the supposed law of Kundt, connecting the wave-length of the absorption band with the value of the dielectric constant of the solvent, is impossible. It is probable that the so-called Melde effect is equally chimerical. Looked at from the point of view of the aggregate theory the Melde effect has very little if any meaning.

Beer's law is found to hold approximately for nearly all solutions of a single neutral salt in a single solvent. Exceptions are found when very concentrated solutions are used, and with only one known exception (solutions of uranyl acetate give a very large negative deviation) the deviation is such that the absorption is greater than would be given by Beer's law when the concentration is increased. The fact that Beer's law holds indicates that, as far as our knowledge of absorption spectra is concerned, there is no difference between ions and molecules. It therefore can not be said, in general, that for solutions showing characteristic bands there is any part of the spectrum due to ions or any part due to molecules. Yet the work of Jones and Anderson[1] showed that certain bands are probably due to certain constituents of the molecules, such as the atom, the hydrate, etc.

A THEORY OF ABSORPTION SPECTRA.

It is natural to try to correlate as many spectra as possible, and this has been done in many cases. For organic compounds, benzene for example, it is found that the ultra-violet absorption spectra in the gaseous, in the liquid, and in the dissolved states are very similar. It is therefore natural to endeavor to test colored salts in the same way. Unfortunately no metallic salts having a characteristic absorption spectrum can be obtained in the gaseous state. As pure salts, in solutions, and in transparent solids, however, the absorption spectra of salts of the same element are very much alike as far as the grosser structure is concerned. None of the vapors of the metals of these salts can be obtained unaccompanied by the effects of high temperature and intense ionization. It is for this reason that the branch of spectroscopy dealing with the absorption spectra of inorganic solutions is quite completely separated from the other branches of spectroscopy.

However, a study of other branches of spectroscopy will be of considerable importance in helping to give us a working hypothesis concerning the material centers that are absorbing or emitting light.

An emission or absorption center of light and heat will be defined as the smallest particle existing by itself that is capable of emitting or absorbing a given characteristic spectrum. Until proved to be an ion, an atom, a molecule or an aggregate of these we can not assume that the division of matter into emission and absorption centers is at all identical with the division of matter into ions, atoms, and molecules. In a study of these light centers one of the most difficult problems that confronts us is the complete separation of individual light centers, and it is owing to this fact that our knowledge of these light centers is so meager. An example of this kind might be taken in the more or less independent series of lines as classified by Kayser and Runge, Ritz, and others. It has never been proved that there are separate emitters and absorbers for each one of these series of lines, neither can it be said that these centers correspond to atomic, ionic, or molecular units. It may be that each series of lines is due to a system, and that several systems are joined together to form an absorption or emission center, but that these systems can not exist as separate units and still act as light centers. The same condition probably applies to the systems that give rise to the simple series of fluorescent bands discovered by Wood, so that there would not be a different absorption center for each one of these series of bands, but that there is one type of absorbing centers that contains several absorbing systems that can be separately excited, and that as soon as the absorbing center is broken into parts it loses its characteristic absorption spectrum.

It seems quite probable that many of the systems in the light centers contain electrons, and it is probable that it is these electrons that give the

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[1] Publication No. 110, Carnegie Institution of Washington.

Zeeman effect. The electrons that are indicated by the Zeeman effect of arc and spark lines are but slightly affected by external forces, so that it has been very generally assumed that these form parts of systems that make up the fundamental structure of the ultimate units of matter. Indeed, a characteristic spectrum has been used as defining an atom; and, in general, it has been found that a characteristic arc and spark spectrum accompanies matter which, according to other physical and chemical methods, is believed to be composed of exactly the same atomic units. It is for this reason that the assumption is generally made that the absorption and emission centers of these arc and spark spectra are either the same as the atoms of the element, or contain one or more atoms of the element.

In making an assumption of this kind two of the greatest difficulties encountered are the complexity of the spectra that are found to be characteristic of an element and the fact that the light centers only seem to exist, or at least are only active under certain conditions. The first problem is answered by supposing that if the light center corresponds to the atomic unit of matter, then there are subatomic systems that correspond to the various spectra. Very little evidence of such subatomic systems is at hand, yet the present theory of radioactivity gives very strong support to this view and indicates that, whenever these subatomic systems are separated, entirely new atomic units are formed, and that one atomic unit may consist of several smaller atomic units. The second problem is illustrated by many examples, a good one being that of sodium. The sodium atoms exist under conditions that make them parts of entirely different light centers. The sodium atom may form part of the absorbing or emitting centers of the arc or spark spectra, the emitting centers of a certain vacuum discharge spectrum, the absorbing centers of the fine-banded absorption spectrum, the emission centers of the fluorescent spectrum, etc. The sodium atoms may also exist in various molecules and be perfectly transparent in the visible part of the spectrum. Suggestions have been made only as to what the constitution of the light centers of these spectra may be, and these suggestions have usually been based on the assumption that these light centers consisted of atomic or molecular complexes.

Most light centers seem to be formed only during very exceptional physical and chemical conditions, so that they have been often considered as being very unstable; and that an atom or molecule only forms a part of a light center during a small part of the time. This view is strengthened by the theory of absorption and dispersion, according to which it often happens that the number of electrons taking part in the absorption or emission of light is much less than the total number of atoms or molecules present in the matter that is either emitting or absorbing the light. Exactly what conditions are necessary for producing light centers? Some evidence has been accumulated which indicates that these conditions may be furnished by the dissociation or recombination of parts that form complex molecules. These are apparently the conditions under which the light centers of the fine iodine, bromine, sulphur, chlorine, etc., bands exist.

The length of duration of the fluorescent and phosphorescent bands of solids and liquids furnishes a method of analysis of spectra in that the duration of different bands after the excitation has ceased is very different. No relations have, however, been found between fluorescence and phosphorescence and the conductivity, so that the current theories are based on the assumption that the light centers are very complex molecular aggregates (Lenard and Klatt) and that the dissociation or recombination effects take place within these aggregates.

The absorption spectra of organic compounds supports the view that the absorbing centers in these cases are generally complex. These centers are called chromophores, and as a rule they form only a part of the molecular structure. Unfortunately the absorption spectra of chromophores are not characteristic, so that the whole study is more or less a colorimetric one. The peculiar conditions under which the absorption centers are active has been assumed to be the same as those accompanying phenomena that are explained by the theory of dynamic isomerism, and consist in a supposed change of the interlinking of radicles in the organic compounds. If valency is of an electromagnetic nature, a condition of dynamic isomerism would also be a condition of intramolecular ionization.

The nature of the absorbing centers of inorganic salt solutions is probably somewhat similar to the absorption centers found in the case of solutions of organic compounds, the phosphorescent compounds of the rare earths studied by Goldstein, Kowalski and others. Every characteristic absorption spectrum will be considered as evidence for the existence of a compound, and these compounds will be called aggregates and may be assumed to consist of one or more molecules or ions of the dissolved salt, and one or more molecules of the solvent. That the number of these aggregates seems to be quite large is no evidence against the theory of aggregates, since there is no reason why an element like uranium should not form a very large number of compounds.

As a typical example of an aggregate, we will take a mixture of two kinds of dissolved compounds in a mixture of two solvents. Assuming that the UO_2 group can act as an ion and that it carries a double charge, a general formula for aggregates would be the following:

$$x\{UO_2SO_4\}\,y\{H_2SO_4\}\,u\{\overset{++}{UO_2}\}\,v\{\overset{+}{H}\}\,w\{SO_4\}\,a\{H_2O\}$$

$$x'\{UO_2SO_4\}\,y'\{H_2SO_4\}\,u'\{\overset{++}{UO_2}\}\,v'\{\overset{+}{H}\}\,w'\{SO_4\}\,b\{CH_3OH\}$$

We may assume that at ordinary concentrations u, v, w, u', v', and w' have small values. Whenever a definite and characteristic absorption spectrum is obtained it will be assumed that the absorption centers are aggregates of a definite composition, and that all the coefficients in the above equation have a definite value.

From the fact that absorption centers are found in solids such as the various glasses and crystals, it must be assumed that the existence of active absorption centers need not be connected with any conducting particles. On the other hand, the work of Becquerel and others seems to indicate that the number of absorbing centers is much smaller than the number of atoms present. If the aggregates are very complex then the number of absorbing centers would be much less than the number of molecules of the colored salt.

This would probably require very large values for x and x', and, therefore, makes this view improbable. On the other hand, it is not necessary to assume that the aggregate is an active light center all the time, but that the aggregate is only active while it is in a peculiar condition. This peculiar condition may be assumed to be a kind of internal ionization, somewhat similar to that which is assumed in the theory of dynamic isomerism, or by the theory of Lenard and Klatt. For instance, electrons may pass back and forth within the UO_2 group, or between the UO_2 and surrounding groups. The system whose vibrations give rise to the uranyl group is probably located in the uranyl radicle, and possibly in the uranium atom itself. When an electron is ejected, or when it recombines with the UO_2 group, it may be considered that the system absorbs light and is then an active center. When this absorption takes place, the frequency of the absorption bands and their width and intensity will depend on the structure of the aggregate—*i.e.*, on the values of x, y, u, v, w, and a.

In a spectroscopic study of the aggregates found in salt solutions, it may be said that the absorption spectrum indicates only a condition of a small part of the salt. In other words, the values of x, y, u, v, w, a, etc., may be functions of the time. In order to solve this problem it will be necessary to study the nature of the aggregates by other methods; and if widely different methods give the same values for x, y, u . . ., etc., it may then be assumed that the value of these variables is not a function of the time.

In the present treatment it will be assumed that these spectroscopic aggregates represent the statistical average condition of the dissolved salt molecules, and although these aggregates may be active absorbing centers for a small part of the time it will be assumed that the difference between an absorbing and a non-absorbing aggregate, if such there be, is not due to any change in the values of x, y, u, v, w, a, etc. The intensity of a given absorption spectrum will be assumed to be a measure of the amount of the aggregate present in the solution that corresponds to the given absorption spectrum. In every known example it has been found that the changes in the values of x, y, z, a, etc., produce changes that indicate that each characteristic spectrum is due to a system whose parts form one organic whole.

SOLVATION.

In the general formula for the structure of the absorbing centers, the coefficient of the solvent part of the compound is represented as being constant. The fact that in the examples studied each solvent is characterized by a definite absorption spectrum, and that a salt dissolved in mixtures of varying proportions of two solvents shows only two definite absorption spectra, indicates that definite compounds of salt and solvent are formed. It is a very remarkable fact that one solvent spectrum does not gradually change into the other solvent spectrum, but that only the relative intensities of the two spectra vary as the percentage of each solvent present is changed, and that for a certain percentage of the two solvents the two sets of solvent spectra are of approximately the same intensity.

Taking as an example uranous bromide in water and methyl alcohol, we have an equilibrium of probably the following type:

$$x\{UBr_4\}a\{H_2O\} \rightleftarrows y\{UBr_4\}b\{CH_3OH\}$$

The variables x and y may be equal and both may be very small. These quantities will be taken up later in the treatment of aggregates.

The fact that there is no gradual shifting of the "water" bands into the "alcohol" bands indicates that the equation representing the equilibrium is not of the type:—

$$a\{UBr_4\}x\{H_2O\}y\{CH_3OH\}$$

where x and y are variable and depend on the amount of water and methyl alcohol present. The above constancy of a and b must not be interpreted too literally, however, as it may be that in the "atmosphere" of solvent molecules only the inner molecules are effective. In this case the constancy of a and b would indicate that only the number of molecules in the outer region of this atmosphere could change, or could consist of a mixture of water and alcohol molecules. Accordingly, the inner solvent atmosphere consists of but a single kind of molecules.

(1) The percentage of solvents for which each set of solvent bands has the same intensity will be used as a measure of the "persistency" of the given solvates. The "persistency" of any given solvate will vary inversely as the proportion of that solvent that is necessary for the bands to appear of a given intensity. Whether there is any relation between the persistency of solvate bands and the absolute values of a and b is not known.

(2) The persistency of the same solvate bands for different salts is quite different. In the case of neodymium chloride in water and alcohol the bands are of the same intensity when 8 per cent of water and 92 per cent of alcohol are present. In the case of samarium chloride a smaller percentage of water is required, the water bands of samarium chloride having a greater persistency than the water bands of neodymium chloride. The persistency of the water bands of neodymium nitrate is different from those of the chloride. In the case of the uranous salts the water bands are much less persistent, the water and alcohol spectra being of about the same intensity when there is about 40 per cent of water and 60 per cent of alcohol present.

(3) The persistency of the bands of the same salt in different solvents is very different. In general the *"water" bands are the most persistent of all the solvent bands at ordinary temperatures.*

(4) The persistency of solvent bands depends on the concentration of the solution. Keeping the percentage of water and alcohol constant, it is found that the alcohol bands of neodymium chloride and of the uranous salts are relatively more persistent for the greater dilutions, *i.e.*, Beer's law does not hold for solutions containing two solvents.

(5) Although it has not been shown that only two solvates exist in the case of a neodymium salt in a mixture of two isomeric solvents, yet there are several instances where the absorption spectra of the same salt in isomeric solvents are very different. A marked example of this kind is that of neodymium chloride in isobutyl and butyl alcohols, the butyl alcohol bands having the shorter wave-lengths. On the other hand, the corresponding propyl alcohol bands are shifted to the red with reference to the isopropyl bands. The absorption of neodymium nitrate in butyl and isobutyl alcohol is very much the same.

(6) From the above examples it must be remembered that because the absorption spectra of a salt in two different solvents prove to be very much the same, this fact is not an argument that no solvation exists in the two cases.

(7) The values of x and y probably have a very considerable effect on the nature of the solvates, but even under these conditions the little work that has been done indicates, for cases where y has a value, *i.e.*, where there are other salts, or the acid corresponding to the given salt is present, that we still have the constants a, b, etc., although these may have a different value from what they have when $y=0$.

(8) Very little work has been done on the change in the persistency of solvate bands when foreign salts are added to the solution. The addition of aluminium and calcium chlorides to solutions of colored chlorides seems to increase the persistency of the alcohol bands relative to the water bands.

(9) The selective action of foreign salts on solvates is shown very strikingly by the addition of oxidizing agents to solutions of uranous salts in water and alcohol. Substances like potassium and calcium nitrates and sodium perchlorate cause the water bands to decrease very greatly in intensity. The alcohol bands, on the other hand, seem to remain of about the same intensity. Whether this is due to the oxidization of the hydrate or simply to a decrease in its persistency, can not always be stated. Some cases indicate that selective oxidization takes place. The oxidization of hydrogen peroxide affects water and alcohol bands in the same way.

(10) In many cases the solubility of a salt like uranous bromide is much less after alcohol has been added to the water than before. Sometimes precipitates form when a second solvent is added, and in some cases the filtrate shows the presence of only one solvate, whereas before the precipitate was formed both solvates were present. This may be denoted as selective solvate precipitation.

(11) The effect of rise in temperature changes the relative intensity of the solvate bands of a solution. A very marked example of this kind is a solution of uranous chloride in a mixture of water and ethyl alcohol in such proportions as to show the water and alcohol bands of the same intensity at ordinary room temperatures. Heat the solution to about 80° C. and the water bands practically disappear, leaving only the uranous alcohol bands in the spectrum.

(12) Whether or not there is a dynamic equilibrium of solvates is not certain, but the selective action of foreign salts, the effect of changing the relative quantities of the solvents and of changing the temperature, would lead us to believe that there is some interchange of solvates going on. The velocity of reactions of this kind may, however, be comparatively slow.

THE URANYL AND URANOUS BANDS.

The uranyl spectrum consists of some twelve bands starting from λ 5000 and runs into the ultra-violet. Starting with the long wave-length band they have been designated by the letters *a*, *b*, *c*, etc. These bands form a series, the distance between the bands decreasing with the wave-length. The uranous bands do not form any series, and resemble the uranyl bands only in their general appearance. The uranium bands are quite wide and diffuse as compared with the erbium and neodymium bands. A considerable amount of confusion has been caused in the past by the fact that most of the uranous salts contain uranyl salts mixed with them, and, therefore, their absorption spectra include the uranyl bands. The complete independence of the two sets of bands is very clearly shown on spectrograms of the absorption spectra of a uranous salt as it is gradually oxidized to the uranyl salt by the addition of hydrogen peroxide.

(1) A problem of considerable interest, and one for which an answer[1] has been partly obtained, is the complete correlation of the *a*, *b*, *c*, etc., bands when one uranyl salt is transformed into another salt, or when the solvent is changed. Thus, for instance, the *a* band could be traced from the nitrate to the sulphate, acetate, etc., and also for these salts in various solvents. It may be that the neodymium, erbium, and samarium bands can be studied in the same manner, especially at low temperatures. The results of such a study should extend very greatly our knowledge of chemical reactions.

(2) If uranyl chloride and calcium nitrate are dissolved in water, uranyl chloride and uranyl nitrate should both be present in the solution. In terms of the theory of aggregates, then, it would be expected that the addition of calcium nitrate to an aqueous solution of uranyl chloride would cause the uranyl chloride bands to shift towards the violet. On the other hand, the addition of aluminium or calcium chloride to an aqueous solution of uranyl nitrate should cause the uranyl nitrate bands to shift towards the red. The experimental results verify these conclusions.

Preliminary spectrograms showed that the addition of calcium nitrate to an aqueous solution of uranyl nitrate caused the uranyl nitrate bands to shift slightly towards the violet, the amount of the shift, however, being very small. This seems to show that calcium itself has very little if any effect upon the absorption, and this is in agreement with the results of Becquerel and others.

(3) When an acid is added to a neutral uranyl salt in sufficient quantity, this salt is changed to a salt of the acid added. Up to the present no quantitative study of the strengths of acids by the spectroscopic method has been made, but by means of radiomicrometric measurements this method should give a reasonably accurate means of measuring the relative strengths of various acids, especially in aqueous solutions.

(4) The *modus operandi* by which uranyl salts are transformed into uranous, and *vice versa*, is not known. This subject has, however, been discussed in the chapter dealing with the spectrophotography of chemical reactions. It seems probable that there is not the usual dynamic equilibrium between the uranyl and uranous salts

AGGREGATES AND THEIR PROPERTIES.

(1) The presence of free acid or of foreign salts[2] has been found to change the frequency of many of the uranyl, uranous, and the neodymium bands. At present our knowledge of these effects is practically restricted to aqueous solutions, although similar effects are known to occur in other solvents. An example of the above effect is that of the uranyl chloride and nitrate bands.

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[1] Publication 130, Carnegie Institution of Washington.

[2] Phys. Zeit., **11**, 668 (1910), **12**, 269 (1911).

The wave-lengths of the uranyl nitrate bands are considerably smaller than those of uranyl chloride. This has been shown to be due to the presence of NO_3 and H_2O groups in the absorbing centers of the nitrate in solution. By adding hydrochloric acid to an aqueous solution of uranyl nitrate, the uranyl nitrate bands shift gradually to the positions of the uranyl chloride bands. The addition of more hydrochloric acid causes most of the uranyl bands to continue to shift towards the red. On the other hand, the addition of nitric acid to an aqueous solution of uranyl nitrate causes the uranyl bands to shift towards the violet. We thus obtain a gradual shifting of the uranyl bands of a nitric acid solution of uranyl nitrate into the position of the uranyl bands of uranyl chloride dissolved in concentrated hydrochloric acid. The magnitude of this shift is shown by the following wave-lengths:

	Uranyl bands.						
	a	*b*	*c*	*d*	*f*	*g*	*h*
Nitrate in nitric acid	4790	4670	4510	4370	4125	4000	3900
Chloride in hydrochloric acid	4950	4800	4635	4450	4280	4050	4015

These changes are quite different as compared with those that take place when the solvent is changed, and if it is assumed that every characteristic absorption spectrum corresponds to a more or less stable system, then the above changes indicate the existence of a series of systems or compounds. These compounds will be called aggregates. There will be, accordingly, nitric acid aggregates of uranyl nitrate, uranyl nitrate and chloride aggregates, and hydrochloric acid aggregates of uranyl chloride.

(2) Whether there is a gradual change in the frequency of vibration of the absorbers for a series of uranyl or uranous aggregates, or whether there is simply a relative change in the intensity of a number of finer bands which blend so as to form the uranyl or uranous bands, can not be decided from the data now in hand. In the case of the neodymium salts, the latter effect seems to manifest itself in the spectrograms that have been made.

(3) It is probable that the presence of free acid in solvents other than water will lead to the discovery of many new bands of neodymium, erbium, etc. A striking example of this kind is the effect of dissolving hydrochloric acid gas in a neodymium chloride solution in ethyl alcohol. The effect of the free acid is to bring out very strongly bands at λ 3695 and λ 3760. The presence of sodium perchlorate has a similar effect.

(4) Mixtures of varying amounts of two salts in the same solvent may result in a gradual shift from the bands of one salt into the bands of the other, the shift depending on the amount of each salt present. As an example of this, uranyl sulphate and uranyl nitrate were studied. On the other hand, there are examples where the two salts do not seem to form any intermediate aggregates, and the bands of each simply vary in intensity without showing any change in frequency.

(5) Acid aggregates of uranous salts are found to be much more stable than the neutral aggregates. Uranous nitrate, for instance, is very unstable; but uranous chloride dissolved in concentrated nitric acid (the absorption spectrum is entirely different from that of uranous chloride) will stand for hours

before it is oxidized to the uranyl condition. Neutral uranous salts in solution, when heated to 80° or 90°, form a black precipitate; but if some free acid is present (or in the case of uranous chloride if other chlorides are present) the uranous salts are much more stable.

(6) Aggregates form compounds with solvents in many cases (for example, various uranous aggregates in water and methyl alcohol) that are as characteristic as those formed by the pure neutral salt. As yet no work has been done on the effect of temperature and concentration on solvate aggregates.

(7) In discussing the differences in the chemical properties of aggregates mention will be made of the reduction and oxidization of uranium salts. It is probable that many other chemical properties differ very much for the various aggregates, but as this work has been mainly concerned with the reduction and the oxidization of the salts, only these properties will be considered. As some of the methods used in the reduction of the uranyl salts are in themselves of considerable interest, they will be taken up in more detail than would otherwise be done.

The method employed for the preparation of the uranous salts for work on absorption spectra has been that described by Jones and Strong.[1] Under these conditions it is possible to obtain quite concentrated solutions of the chloride, the bromide, and the sulphate. No aqueous solution of uranous nitrate could be obtained, although small amounts would be formed when the hydrogen was first liberated from the acid, but in a very short time the uranous nitrate was oxidized.

The most concentrated solution of any uranous salt thus far obtained is that of the chloride. Uranyl chloride is dissolved in ether (the solution forms three distinct, unmiscible layers, the concentration of uranyl chloride in each being different). To this solution is added a small amount of zinc and concentrated hydrochloric acid. The uranous chloride formed is insoluble in ether and accumulates in the dark oily liquid at the bottom of the vessel. Layers of this liquid 1 mm. thick are almost opaque. The reduction of uranyl chloride in isobutyl alcohol is very similar to that in ether.

When hydrochloric acid and zinc are added to a solution of uranyl nitrate a considerable amount of a uranous salt is formed, although it is quickly oxidized again. This is true even when quite large amounts of hydrochloric acid are present. A much more complete spectrographic study of the reduction of uranyl aggregates should be made, as it would probably lead to some knowledge as to how the oxygen atoms are removed from the uranyl group and the influence the other atoms and molecules of the aggregate have upon this reduction.

(8) Oxidization reactions also indicate very clearly that different aggregates apparently possess different properties, although the action of the other salts or acids present in the solution may modify the action of the oxidizing agent. However this may be, it is found that uranous acid aggregates require a great deal more of the oxidizing agent, especially when this is hydrogen peroxide, than do the neutral aggregates.

(9) Assuming the presence of aggregates, it is important to know what effect dilution has upon their composition. It would be supposed that the aggregates would break down at high dilution. To test this supposition the

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[1] Phil. Mag., 19, 566 (1910)

absorption spectra of uranyl nitrate and uranyl sulphate were photographed at very great dilution. If dissociation is sufficiently complete it would be expected that the uranyl nitrate bands would shift towards the red with decrease in concentration, and the uranyl sulphate bands would shift towards the violet, so that for very great dilution the uranyl bands of both salts would be identical. This was not found to be the case. There appeared a very slight shift of the uranyl nitrate bands to the red, and possibly a slight shift of the uranyl sulphate bands to the violet; but these shifts were extremely small; so small, indeed, that some observers who looked at the spectrograms did not detect it at all. If the shifts occur, it is exactly what would be expected if the uranyl nitrate and uranyl sulphate aggregates break up into complex ions. The loss of an NO_3 group would cause the uranyl nitrate bands to shift only slightly to the red if the aggregate was of some size, and the same would be true of the uranyl sulphate aggregate. If this theory is true it indicates that the aggregates possess quite a high degree of complexity.

(10) The question has been asked as to whether the aggregates are definite chemical compounds, whether they have a definite composition, and how stable they are. Unfortunately the spectroscopic method itself can not solve these problems, but by studying the composition of the acid aggregate precipitates that are often formed, and the chemical composition and absorption spectra of these, much light may be thrown on the subject. The other physical and chemical properties of solutions containing aggregates should also be studied.

THE EFFECT OF TEMPERATURE ON ABSORPTION SPECTRA.

(1) The general effect of rise in temperature is to give a solution of an inorganic salt a deeper color. This deepening of the color signifies that the absorption of light has become more selective, and spectroscopic work indicates that this selective absorption is usually due to a widening of the absorption bands. As these bands are never so distributed over the spectrum as to give a colorless solution, it follows that a widening of the absorption bands will intensify the color of the solution. In many cases this widening appears to be quite unsymmetrical, but this need not necessarily mean that the center of gravity of the individual absorption band is shifted. Many examples of the neodymium absorption bands show this phenomenon very clearly. For instance, the absorption due to the γ and δ groups of bands may be sufficiently intense to make these groups appear as single bands. If the absorption is not so intense as this, in some solvents it is found that with rise in temperature the shortest wave-length bands may decrease in intensity, and may even disappear. The long wave-length bands increase in intensity, and in some cases new bands appear. Knowing this, it is easy to understand that if the absorption is so strong that each of these groups of bands appears as a single band, these broad bands will widen very unsymmetrically towards the red with rise in temperature. It may be that some change like this takes place in the case of the uranyl bands. It is for this reason that a formula calculated for the widening of a band with rise in temperature would not apply to many wide bands.

(2) In the case of all pure salts dissolved in a single solvent, the bands have been found to widen with rise in temperature, and at the same time the

bands become more diffuse, the edges becoming hazier. When there is a mixture of salts in the same solvent, the bands may become much weaker with rise in temperature. This is the case in a mixture of neodymium and calcium chlorides in water. In a similar manner the absorption of a salt in two solvents probably decreases in intensity with rise in temperature. An example of this kind is that of uranous bromide in 40 per cent water and 60 per cent alcohol. At ordinary temperatures the bands are of about equal intensity. At 80° the water-bands have practically disappeared, without the alcohol bands having widened to any great extent.

(3) In general the center of intensity of single bands changes but little. Whenever there is any change of wave-length, the shift is invariably towards the red. It seems that this shift is greater the wider the band, so that it is difficult to say in most cases whether the shift is real or only apparent. In the case of solutions of pure neodymium and erbium salts the shift is, in general, too small to be observed.

(4) A study of gaseous aggregates such as $N_2O_4 \rightleftarrows 2NO_2$ indicates that raising the temperature or lowering the pressure increases the relative number of the simpler molecules. Many vapors like those of the fatty acids show molecular clustering at low temperatures. In a similar manner it would be expected that aggregates would gradually break down at the higher temperatures. In considering specific examples, it would be expected that acid uranyl sulphate aggregates in breaking down would result in a shift of the uranyl bands, the shift being towards the violet. On the other hand, if the nitric acid uranyl nitrate aggregates are broken down, it would be expected that the uranyl bands would be shifted towards the red. According to this view the shift of the uranyl bands of uranyl nitrate in nitric acid and of uranyl sulphate in sulphuric acid, with rise in temperature, should be quite different if the only effect of rise in temperature is a breaking up of the aggregates.

In advancing an hypothesis of this kind it is assumed that it is only the molecules in an aggregate that are effective in changing the frequency of vibration of the absorbing systems of the light centers. This means that the kinetic energy of the aggregate corresponds to that of a molecule at the same temperature in the solution, the individual molecules in an aggregate all moving together. Whether there is a constant interchange of these molecules and the molecules of the solution, spectroscopic evidence does not as yet show. Neither can it be said with certainty that molecules outside the aggregates do not affect the frequencies of vibration of the absorbing system within the aggregate. Assuming that this is not the case, then it follows of necessity that with rise in temperature the acid aggregates are not broken up, because the uranyl bands of acid solutions are then shifted to the red. This shift seems to be about as great for uranyl sulphate in sulphuric acid as it is for uranyl nitrate in nitric acid. In a similar manner, acid solutions of neodymium salts do not have their absorption spectra changed so as to resemble more closely that of the neutral salt, with rise in temperature, as one would expect if the acid neodymium aggregates were broken down.

(5) When foreign salts like calcium chloride are added to solutions of neodymium chloride, it is probable that aggregates containing the two salts are formed. In the case of aqueous solutions of these salts it is found that

the neodymium bands are shifted to the red with rise in temperature, whereas aqueous solutions of pure neodymium chloride do not show this effect at all. Exactly what takes place in this case is not evident.

(6) The effect of rise in temperature on solutions showing the solvate bands of equal intensity has been to cause a change in the intensity of the solvate bands; very little if any change, however, in the wave-lengths of the bands takes place. In the case of water and alcohol, the alcohol bands increase in persistency as the temperature is raised.

(7) In the work with the closed cell at high temperatures it was found that precipitates were formed in practically every case, probably due to hydrolysis, alcoholysis, etc., precipitation taking place in dilute as well as in concentrated solutions. Several examples were tested of concentrated solutions of colored salts mixed with calcium or aluminium chloride, and precipitation was found to take place under these conditions at comparatively low temperatures. It would be very interesting to learn whether acid aggregates of uranyl, neodymium, erbium and such salts are less likely to form precipitates than the neutral salt solutions.

In the case of neutral uranous solutions these precipitates form at 70° or 80°. The presence of acid prevents this precipitation at temperatures below 100°.

Whether the salt precipitation at high temperatures is complete or not, can not be decided in general at present. In the case of several neodymium and erbium solutions this seemed to be the case. In one of the uranyl solutions, however, some uranyl salt remained in the solution after the precipitate had settled.

(8) It may be said, in general, that there is a very great increase in the absorption of all solutions in the short wave-length region of the spectrum as the temperature is raised. How great this increase in absorption would be if pure solutions were used has not yet been determined. The formation of precipitates is usually preceded by a very great increase in the short wave-length absorption.

(9) The problem as to whether a rise in temperature produces a permanent change in the structure of the aggregates in solution has not been studied to any great extent. In the case of the existence of two solvent spectra it is found that the spectra on cooling the solution are exactly the same as before heating. In the case of an acetone solution of uranyl chloride it was found that the bands are apparently single after the precipitate was formed during the heating. Whether these bands would have become double again when the solution was cooled was not tested. It would be interesting to learn whether selective solvate precipitation would take place on heating solutions.

(10) It seems worth while in conclusion to call attention to the promising and important application of spectrophotography at low temperatures to the study of the nature of chemical reactions. As soon as the changes in breadth, intensity, and frequency of individual absorption bands and the constitution of the groups of bands can be interpreted, our knowledge of the relation between absorption centers or aggregates and the other physical and chemical units of matter will be much more fully understood; and the changes which these particles undergo will be much better comprehended.

DESCRIPTION OF PLATES.

With the exception of the plates representing changes in temperature of the solution, the times of exposure and the width of the slit are the same for each strip of the plate. The current through the Nernst glower was kept constant. In the case of the uranyl salts a much longer exposure is often made in the ultra-violet and violet, in order to bring out the uranyl bands as strongly as possible, and this will be noted in the description. In some strips ultra-violet wave-length spark lines will be found, these being photographed without the solution in the path of the light, and only for purposes of measurement. In exposures to the spark of this kind, the film holder was never moved between the photographing of the absorption spectra of the solution and that of the spark spectra. In some instances the strips are not uniformly exposed. This was due in many cases to the formation of precipitates. A great deal of trouble of this kind was encountered, especially with the uranous salts, in the high temperature work, and in the spectrophotography of chemical reactions. In referring to the strips, the first or lowest strip will be that at the bottom of the plate—the one that is nearest the scale of wave-lengths. The scale of wave-lengths is in Ångström units, the whole number standing for so many hundred Ångström units.

Plate 1. *A.* Lithium Chromate in Water. Depths of cell and concentrations, starting with the lowest strip: 0.25 normal, 3mm.; 0.25 normal, 24 mm.; 0.46 normal, 24 mm.; 1.0 normal, 24 mm.; 1.5 normal, 24 mm.; and 2.0 normal 24 mm.

B. Lithium Bichromate in Water. Depths of cell and concentrations, starting with the lowest strip: 0.25 normal, 3 mm.; 0.25 normal, 24 mm.; 0.46 normal, 24 mm.; 1.0 normal, 24 mm.; and 2.0 normal, 24 mm.

Plate 2. *A.* Calcium Ferricyanide in Water. Depth of cell kept constant, 24 mm. Concentrations, starting with the lowest strip, 0.031, 0.058, 0.125, 0.175, and 0.25 normal.

B. Calcium Ferrocyanide in Water. Depth of cell kept constant, 24 mm. Concentrations, starting with the lowest strip, 0.25, 0.46, 0.66, 1.0, 1.5, and 2.0 normal.

Plate 3. *A.* Aluminium Chromate in Water. Depths of cell, 3, 24, 24, and 24 mm. Concentration could not be determined on account of hydrolysis.

B. Calcium Chromate in Water. Depth of cell constant, 24 mm. Concentration somewhat less than 0.01 normal.

Plate 4. *A.* Copper Bichromate in Water. Depths of cell and concentrations, starting with the lowest strip: 3 mm., 0.044 normal; 24 mm., 0.044 normal; 24 mm., 0.08 normal; 24 mm., 0.117 normal; 24 mm., 0.175 normal; 24 mm., 0.26 normal; and 24 mm., 0.35 normal.

B. Potassium Nickel Chromate in Water. The depth of cell was kept constant at 24 mm., and the concentration could not be determined on account of hydrolysis.

Plate 5. *A.* Neodymium Chloride in Butyl Alcohol. Depth of cell 10 cm. and concentration 0.024 normal, strip 1, and in Butyl Alcohol, depth of cell 3 cm. and concentration 0.04 normal, strip 2.

B. Neodymium Chloride in Glycerol and Ethyl Alcohol, concentration constant, 0.5 normal. Depth of cell constant, 18 mm.; starting with the lowest strip the following numbers represent the percentage of the solvents:

10, 15, 20, 40, 60 glycerol.
90, 85, 80, 60, 40 ethyl alcohol.

Plate 6. *A.* Neodymium Chloride in Isopropyl Alcohol. Depth of cell 30 mm. Concentration, 0.0266 normal.

B. Neodymium Nitrate in Tertiary Butyl Alcohol. Concentration, 0.2 normal.

C. Neodymium Chloride in Water and Alcohol. The lower strip represents about 8 per cent water and shows both sets of bands. Concentration, 0.5 normal. The other strips show the effect of adding hydrogen peroxide.

PLATE 7. *A*. Neodymium Chloride in Propyl Alcohol. Depth of cell constant, 30 mm. Concentrations, starting with lowest strip, 0.04, 0.03, 0.02, and 0.0133 normal.

B. Neodymium Nitrate in Propyl Alcohol. Depth of cell constant, 16 mm. Concentrations, starting with lowest strip, 0.05, 0.07, 0.10, 0.15, 0.225, and 0.3 normal.

PLATE 8. *A*. Neodymium Chloride in Isobutyl Alcohol. Depth of cell constant, 34 mm. Concentrations, starting with lowest strip, 0.024, 0.018, 0.012, and 0.008 normal.

B. Neodymium Nitrate in Isobutyl Alcohol. Depth of cell, 16 mm. Concentrations, starting with lowest layer, 0.05, 0.07, 0.10, 0.15, 0.225, and 0.3 normal.

PLATE 9. *A*. Neodymium Nitrate in Butyl and Isobutyl Alcohols. Strip 1 is a 3 mm. and strip 2 a 13 mm. layer of a 0.3 normal solution in butyl alcohol; strip 3 is a 3 mm. and strip 4 a 13 mm. layer of a 0.6 normal solution in isopropyl alcohol.

B. Neodymium Nitrate in mixtures of Ethyl and Isobutyl Alcohols. Depth of cell constant, 34 mm. Concentration constant, 0.1 normal. Starting with lowest strip the percentages of the solvents were:

20, 40, 60, 80, 100 ethyl alcohol.
80, 60, 40, 20, 0 isobutyl alcohol.

PLATE 10. *A*. Neodymium Nitrate in Methyl Ester. Depth of cell constant, 18 mm. Concentrations, starting with lowest strip, 0.05, 0.07, 0.10, 0.15, 0.225, and 0.3 normal.

B. Neodymium Nitrate in Ethyl Ester. Depth of cell constant, 18 mm. Concentrations, starting with lowest strip, 0.05, 0.07, 0.10, 0.15, 0.225, and 0.3 normal.

PLATE 11. *A*. Neodymium Nitrate in Anthracene and Ethyl Acetate. The variable quantity here is depth of cell. The early investigators made experiments to test whether two colored salts in the same solvent having bands that were of almost the same wave-lengths had the wave-lengths of these bands changed with reference to the wave-lengths of the bands for the solutions of the separate salts. At present this would hardly be expected to result, unless double solvates were formed, *i.e.*, compounds containing the two salts and the solvent. This spectrogram was taken to find whether the anthracene and neodymium bands had their wave-lengths affected by both being dissolved in ethyl ester. This might be expected if compounds were formed containing both anthracene and neodymium nitrate. The bands are in the ultra-violet. Unfortunately it is very difficult to obtain the anthracene and neodymium bands together.

B. Neodymium Nitrate in Ethyl Acetate and Anthracene. To obtain this spectrogram it was necessary to heat the solutions in order to keep the anthracene in solution. The percentages of anthracene for the 6 strips, starting with the lowest, were: 0.25, 0.5, 0.75, 1, 1.5, and 2.

PLATE 12. *A*. Neodymium Nitrate in Ethyl Acetate and Anthracene. Concentration of neodymium nitrate, 0.24 normal. Succeeding strips show the effect of adding ethyl alcohol, methyl alcohol and acetic acid, respectively.

B. Neodymium Nitrate in Ethyl Acetate and Anthracene. The lowest strip is the only one that shows the anthracene bands.

PLATE 13. *A*. Neodymium Acetate in Formamide. The acetate slowly decomposes, forming a white precipitate. Strips 1 and 2 represent different depths of cell (strip 2 being 35 mm.). Strip 3 is the same as 2 after water has been added. The original film shows quite a large shift of the neodymium bands towards the violet in the upper strip, compared with the second strip.

B. Uranyl and Uranous Sulphates in Water, to which Acetic Acid is added. Starting with strip 1 increasing amounts of acetic acid are added to an aqueous solution of uranyl sulphate. This results in a precipitate (strip 5), and the solution is filtered and the absorption spectra again taken (strip 6). Strips 7 and 8 represent the uranous salt formed from the solution used for strip 6 when zinc is added.

PLATE 14. *A*. Uranyl Chloride in Isopropyl Alcohol. Concentration of the chloride, 0.005 normal. Depth of cell variable.

B. Uranyl Chloride in Ethyl Acetate. Depths of cell, starting with lowest strip, 12, 24, 24, 24, 24, 24, 24, and 24 mm. Concentrations, 0.075, 0.075, 0.01, 0.014, 0.02, 0.03, 0.045, and 0.06 normal.

PLATE 15. *A*. Strip 1 is the absorption of a solution 35 mm. deep of Uranyl Nitrate in Methyl Ester. Strip 2 is the absorption of Erbium Chloride (35 mm.) in Propyl Alcohol. The other strips represent the absorption of Uranyl Chloride in Butyl Alcohol.

B. Uranyl Chloride in Formamide. Depths of cell, 3, 15, 15, 15, 15, and 15 m. Respective concentrations, 0.073, 0.073, 0.1, 0.147, 0.219, and 0.293 normal.

PLATE 16. *A*. Uranyl Chloride in Water, to which increasing amounts of an aqueous solution of Calcium Nitrate are added. This spectrogram was made to determine whether the addition of calcium nitrate resulted in a gradual shift of the uranyl bands. The original film shows that the A and B bands decrease in intensity, and the decrease seems to be considerably greater on the red side of the bands.

B. Uranyl Nitrate in Nitric Acid, to which increasing amounts of a concentrated aqueous solution of Aluminium Chloride are added. The first addition consisted of three drops, and shows a large shift of the uranyl bands towards the red. A gradual shift towards the red is shown by the succeeding strips in the original film.

PLATE 17. *A*. Uranyl Nitrate in Nitric Acid to which increasing amounts of Hydrochloric Acid are added.

B. Uranyl Nitrate in Water to which an aqueous solution of Aluminium Chloride is added. This spectrogram shows very clearly the shift of the uranyl bands towards the red.

PLATE 18. *A*. Uranous Chloride in Propyl Alcohol. The variable here is the depth of cell.

B. Uranyl Chloride in Propyl Alcohol. Depths of cell, 3, 12, 24, 24, 24, 24 and 24 mm. Respective concentrations, 0.025, 0.025, 0.033, 0.046, 0.06, 0.1, 0.15, and 0.2 normal.

PLATE 19. *A*. Uranous Chloride in Isobutyl Alcohol.

B. Uranyl Chloride in Isobutyl Alcohol. Starting with strip 1 the depth of cell was 10 mm.; succeeding depths were 24 mm. The corresponding concentrations were: 0.02, 0.027, 0.037, 0.053, 0.08, 0.12, and 0.16 normal.

PLATE 20. *A*. Uranous Chloride in Isobutyl Alcohol. When uranyl chloride in isobutyl alcohol is reduced by the addition of zinc and a small amount of concentrated hydrochloric acid, the uranous chloride formed appears as dark green, oily looking drops, which collected at the bottom of the solution. The remainder of the solution dissolves only a very small portion of the uranous chloride. 19 A represents the absorption of the dilute portion; whereas this plate represents the absorption of very thin layers of the concentrated solution of uranous chloride.

B. Uranyl Chloride in Methyl Ester. Starting with strip 1 the depths of cell and concentration were: 10 mm., 0.021; 24 mm., 0.028; 24 mm., 0.04; 24 mm., 0.057; 24 mm., 0.085; 24 mm., 0.13; and 24 mm., 0.17 normal.

PLATE 21. *A*. Uranous Chloride in Propyl Alcohol.

B. Uranyl Nitrate in Propyl Alcohol. Strip 1 has a depth of cell of 10 mm. and the depth for the other strips is 24 mm. The concentrations were 0.08, 0.10, 0.15, 0.21, 0.32, 0.48, and 0.63 normal.

PLATE 22. *A*. Uranyl Nitrate in Water to which increasing amounts of Calcium Nitrate were added. The addition of calcium chloride would cause the uranyl bands to be shifted towards the red. If this is due to the presence of calcium, then calcium nitrate should also cause the uranyl bands to shift towards the red. This does not appear from the plate, the bands being practically of the same wave-lengths after calcium nitrate had been added. This spectrogram (the film at least) gives evidence that the effective agent in causing the shifts of the uranyl bands is the acid radicle.

B. Uranous Chloride in Ether and Hydrochloric Acid to which Acetone is added.

Plate 23. *A*. Uranous Bromide in Water to which Methyl Alcohol is added. This spectrogram shows the great difference between the water and methyl alcohol bands of uranous bromide.

B. Uranous Chloride in Water to which Methyl Alcohol is added. The methyl alcohol was added in smaller quantities than to the solutions whose spectrograms are recorded in the above plate.

Plate 24. *A*. Uranous Chloride in Methyl Ester to which Water is added.

B. Uranous Chloride in Methyl Ester. Depth of cell is gradually increased.

Plate 25. *A*. Uranous Chloride in Ethyl Ester. Depth of cell variable.

B. Uranous Acetate in Acetone. Depth of cell variable.

Plate 26. *A*. Uranous Chloride in Ether. Depth of cell variable.

B. Uranous Chloride in Acetone. Depth of cell variable.

Plate 27. *A*. Uranous Chloride in concentrated Nitric Acid. The uranous chloride is added to the acid which was placed in the Uhler cell. It is very remarkable that the uranous salt is not oxidized under these conditions.

B. Uranous Bromide in Water and Methyl Alcohol after the precipitate has been filtered off (strip 1). This shows a selective precipitation of the hydrate. The succeeding strips show the absorption of uranous bromide in water and methyl alcohol to which increasing amounts of nitric acid (in the same proportion of water and alcohol) are added.

C. Uranous Chloride in Propyl Alcohol to which Acetone is gradually added.

Plate 28. *A*. Gadolinium Chloride in Ethyl Alcohol. Concentration constant, 0.8 normal. Depths of cell, starting with the lowest strip, 2, 4, 9, 18, 27, and 27 mm. In the upper strip an exposure was made directly to the ultra-violet spark lines.

B. Gadolinium Chloride in Water. Concentration constant, 1.407 normal. Depths of cell, starting with the lowest strip, 2, 10, 15, 22, 22, and 100 mm. In the upper two strips an exposure was made directly to the ultra-violet spark lines.

Plate 29. *A*. Dysprosium Chloride in Methyl Alcohol. Concentration about normal. In all the spectrograms of gadolinium, dysprosium, and samarium, the slit width was 0.10 mm., the current in the Nernst glower 0.9 ampere, and the length of exposure was 1 minute to the visible portion of the Nernst glower spectrum, and about 5 minutes to the ultra-violet part of the Nernst glower spectrum. The depths of cell were 1, 5, 12, 20, 31, and 31 mm. The upper strip was exposed directly to the ultra-violet spark lines.

B. Dysprosium Chloride in Water. Concentration, 1.86 normal. Depths of cell, starting with lowest strip, 2, 6, 10, 15, 21, and 100 mm. All the strips except the lowest one were exposed directly to the ultra-violet spark lines.

Plate 30. *A*. Dysprosium Chloride in Water. Concentration, 1.86 normal. Depths of cell, starting with lowest strip, 2, 8, 16, and 21 mm.

B. Dysprosium Acetate in Water to which varying amounts of Nitric Acid were added. Concentration of the neutral solution, 0.4 normal. The increased depth of cell is due to the addition of concentrated nitric acid. Starting with the lowest strip the depths of cell were: 15, 15.1, 15.3, 15.7, 16.7, and 32 mm.

Plate 31. *A*. Dysprosium Acetate in Water. Concentration, 0.4 normal. Depths of cell, starting with lowest strip, 4, 16, 25, and 34 mm. Exposures were made in strips 2, 3, 5 directly to the ultra-violet spark lines.

B. Dysprosium Chloride in Ethyl Alcohol. Concentration, 0.74 normal. Depths of cell, 2, 10, 15, 24, 30, and 30 mm. The upper strip was exposed directly to the ultra-violet spark lines.

Plate 32. *A*. Samarium Chloride in Water. Concentration, 1.31 normal. Depths of cell, starting with lowest strip, 2, 6, 12, 16, 20, and 100 mm. Strips 3, 4, 5, 6 were exposed directly to the ultra-violet spark lines.

B. Samarium Chloride in Methyl Alcohol. Concentration about normal. Depths of cell, 2, 5, 9, 18, 27, and 27 mm. The upper strip was exposed directly to the ultra-violet spark lines.

PLATE 33. *A*. Samarium Nitrate in Water. Concentration, 1.06 normal. Depths of cell, 1, 4, 12, 22, and 22 mm. Strips 3 and 5 were exposed directly to the ultra-violet spark lines.

B. Samarium Chloride in Ethyl Alcohol to which Water is gradually added. The first strip represents the absorption of a 0.9 normal aqueous solution of 5.5 mm. depth. To this solution were added small amounts of water, so that the depths of cell were 5.5, 5.6, 5.7, 5.9, 6.0, 6.2, and 6.4 mm. The change from the first to the second strip represents a change from the alcohol to the water spectra. After the second strip there is very little change in the spectrum.

PLATE 34. *A*. Samarium Chloride in Ethyl Alcohol. Concentration, 0.9 normal. Depths of cell, 1, 4, 9, 18, 25, and 25 mm. The upper strip was exposed directly to the ultra-violet spark lines.

B. Samarium Chloride in Ethyl Alcohol to which Water is added. The first strip represents the absorption of a 0.09 normal solution in ethyl alcohol. Succeeding strips represent the absorption of the same solution to which small quantities of water have been added. Starting with the lowest strip the depths of cell were: 18, 19, 20, 21.5, 22.5, 25, and 28 mm.

PLATE 35. *A*. Cobalt Bromide in Methyl Alcohol. Concentration, 0.2 normal. Depth of cell, 1.0 cm. Current in the Nernst glower 0.8 amperes. Strip 1 was exposed 4 minutes to the visible, and 4 minutes to the violet and ultra-violet, the temperature being 29° C. Strip 2 was exposed 6 minutes to the whole spectrum, at 44°. Strip 3 was exposed 6 minutes at 57°, and strip 4, 15 minutes at 70°.

B. This spectrogram shows the gradual oxidization of an aqueous solution of Uranous Sulphate to which small amounts of Hydrogen Peroxide have been added. The plate shows the gradual decrease in intensity of the uranous bands, and the corresponding increase in intensity of the uranyl bands. A spectrogram of this kind makes it very easy to differentiate between the uranous and the uranyl bands.

PLATE 36. *A*. This plate represents the absorption of an acidified solution of Uranous Chloride, dissolved in equal volumes of Water and Methyl Alcohol (strip 1) to which was added a concentrated solution of Calcium Nitrate dissolved in two parts of Water and three parts of Methyl Alcohol (succeeding strips). The original film shows very clearly the selective action of the calcium nitrate on the water and alcohol bands, the water bands becoming much weaker, whereas the alcohol bands remain of about constant intensity.

B. Uranous Acetate in Water to which Nitric Acid is added. The first four strips represent uranous acetate in water for different depths of cell, the depth of cell in strip 4 being 2.0 cm. The succeeding strips show the absorption of the same solution as that used in strip 4, increasing amounts of nitric acid having been added. This spectrogram is then a spectrograph of the transformation of uranous acetate into uranous nitrate, and then the oxidization of uranous nitrate to uranyl nitrate.

PLATE 37. *A*. Uranous Chloride in Water to which increasing amounts of Nitric Acid are added. The first strip was accidentally exposed a short time directly to the Nernst glower. This is a spectrophotograph of the chemical reaction represented by uranous chloride being converted into uranous nitrate.

B. Uranous Chloride in equal parts of Water and Methyl Alcohol (strip 1) to which Nitric Acid is added (strips 2, 3, and 4), and to which Hydrogen Peroxide is added (strip 5). This spectrogram shows how the water and alcohol bands of uranous chloride are changed to the nitrate bands, and how these in turn are replaced by the uranyl nitrate bands. The uranous nitrate bands are seen to be very different from the chloride bands.

Plate 38. *A*. Uranous Chloride in equal parts by volume of Water and Methyl Alcohol (strip 1) to which is added increasing amounts of Sodium Chlorate dissolved in equal volumes of Water and Methyl Alcohol (succeeding strips). This spectrogram shows very little of any selective action on the uranous chloride water and alcohol bands.

B. Uranous Chloride in equal volumes of Water and Methyl Alcohol (strip 1) to which Potassium Chlorate in Water and Methyl Alcohol is added in increasing amounts (strips 2, 3, 4, and 5), and to which Hydrogen Peroxide is added (strip 6). This spectrogram shows the selective action of potassium chlorate on the uranous chloride water and methyl alcohol bands. The water bands are seen to decrease in intensity, while the alcohol bands increase in intensity. In this example the addition of hydrogen peroxide seems to have oxidized only the alcoholated uranous chloride.

Plate 39. *A*. Uranous Chloride in equal volumes of Water and Methyl Alcohol (strip 1) to which is added Sodium Chlorate in equal volumes of Water and Methyl Alcohol (strip 2) in one case, and Potassium Chlorate in the other (strip 3). The last strip represents the absorption of uranous chloride in methyl alcohol and ether. This plate shows the selective action of the above salts on the water and alcohol bands.

B. Uranous Chloride in equal volumes of Water and Alcohol to which is added Calcium Nitrate in 2 parts Water and 3 parts Methyl Alcohol (strip 1); in 1 part Water and 1 part Methyl Alcohol (strip 2); and in pure Water (strip 3). A corresponding addition of potassium nitrate was made, the potassium nitrate being dissolved in 2 parts water and 3 parts methyl alcohol (strip 4), 1 part water and 1 of alcohol (strip 5) and in pure water (strip 6). The last strip represents the absorption of uranous chloride itself in equal parts of water and methyl alcohol. This spectrogram shows the selective action of the salts on the uranous water and alcohol bands. The selective action is particularly marked in the case of potassium nitrate. The presence of this salt seems to weaken the alcohol bands much less than the water bands, the proportion of water and alcohol present being kept constant.

Plate 40. *A*. Uranous Bromide in Water to which Methyl Alcohol is added. The concentration of the aqueous solution was 0.5 normal, and the percentages of alcohol in the solution, starting with the first strip, were: 0, 24, 39, 49, 56, and 62. This spectrogram shows that in the case of uranous bromide at this temperature and concentration (the solution also contains zinc bromide) it is necessary that the amount of alcohol required to make the water and alcohol bands have approximately the same intensity is about 1½ times that of the water present.

B. Uranous Chloride in acidified (Hydrochloric Acid) Ethyl Ester to which Ethyl Alcohol is added. The absorption of the ester solution is very similar to that of an aqueous solution. The spectrogram shows the much greater absorbing power of the ethyl alcohol solution compared with the ester solution, the amount of uranous chloride being kept constant.

Plate 41. *A*. Uranous Chloride in Water and Methyl Alcohol (strip 1) to which are added increasing amounts of Calcium Nitrate in 2 parts Water and 3 parts Methyl Alcohol (strips 2, 3, 4), and finally Hydrogen Peroxide (strip 5). The spectrogram shows that the original solution was almost entirely free from uranyl chloride; that the addition of calcium nitrate had a marked selective action on the uranous bands, the water bands being greatly decreased in intensity while the alcohol bands became more intense. The addition of hydrogen peroxide causes the complete disappearance of the uranous bands and the appearance of the uranyl bands.

B. Uranous Bromide in 2 parts Water and 3 parts Methyl Alcohol (strip 1) to which Hydrogen Peroxide (2 parts of a 3 per cent Hydrogen Peroxide solution in Water with 3 parts of Methyl Alcohol) was added 5 drops at a time (strips 2, 3, 4, 5, 6, and 7). Strip 1 shows that the oxidization of the uranous chloride by the hydrogen peroxide is the same, as indicated either by the intensity of the water bands or the alcohol bands.

PLATE 42. *A*. Uranous Bromide in 7 parts Water and 12 parts Methyl Alcohol (strip 1) to which are added 10 (strip 2), 20 (strip 3), 40 (strip 4), and 80 (strip 5) drops of a concentrated solution of Calcium Nitrate in Water. This spectrogram shows that in this case the water bands are intensified and also changed in character, the two red water bands having their relative intensities greatly changed. The percentages of water present, starting with strip 1, were: 37, 43, 52, 64, and 75.

B. Uranous Chloride in Ether and Methyl Alcohol to which increasing amounts of Hydrogen Peroxide were added.

PLATE 43. *A*. Uranous Chloride in Water and Methyl Alcohol to which Hydrogen Peroxide is gradually added. This spectrogram shows the simultaneous oxidization of the hydrate and alcoholate of uranous chloride.

B. Uranous Bromide in Water and Methyl Alcohol to which Potassium Chlorate in Water and Methyl Alcohol was gradually added.

PLATE 44. *A*. Uranous Chloride in Water and Acetone to which Hydrogen Peroxide is gradually added.

B. Uranous Bromide in Glycerol to which Hydrogen Peroxide is gradually added.

PLATE 45. *A*. Uranous Bromide in Water and Methyl Alcohol to which Nitric Acid is added.

B. Uranous Chloride in Acetone and Methyl Alcohol to which Nitric Acid is added.

PLATE 46. *A*. Uranous Bromide in 7 parts Water and 12 parts Methyl Alcohol (strip 1) to which is added Potassium Nitrate in 2 parts Water and 3 parts Methyl Alcohol (strips 2 and 3), and corresponding strips (4, 5, and 6) where Calcium Nitrate is added instead of Potassium Nitrate. This spectrogram shows the selective action of these salts on the water and alcohol bands, the water bands having practically disappeared in strips 3 and 6.

B. Uranous Sulphate in Water to which Nitric Acid is added in increasing amounts.

PLATE 47. *A*. Uranous Bromide in 7 parts Water and 12 parts Methyl Alcohol to which increasing amounts of Calcium Nitrate in Methyl Alcohol are added.

B. Uranous Bromide in 2 parts Water and 3 parts Methyl Alcohol to which increasing amounts of Sodium Perchlorate in Methyl Alcohol are added. These strips of A and B show the selective action of the calcium nitrate and sodium perchlorate on the water and alcohol bands, the water bands practically disappearing. In this case part of the effect may be due to the increased percentage of alcohol present.

PLATE 48. *A*. Uranous Sulphate in Sulphuric Acid to which Nitric Acid is added. No oxidization takes place.

B. Uranyl Bromide in Water to which Nitric Acid is added. The two upper strips represent the absorption of a solution of uranyl chloride to which were added acetic acid and zinc, to find whether uranous acetate or uranous chloride would be formed, and in what amounts.

PLATE 49. *A*. Uranous Bromide in Water and Methyl Alcohol.

B. The first three strips represent the oxidization of an aqueous solution of Uranous Sulphate by Hydrogen Peroxide. The other four strips represent the oxidization of a Sulphuric Acid solution of Uranous Sulphate by Hydrogen Peroxide.

PLATE 50. *A*. Cobalt Chloride in Methyl Alcohol. Concentration, 0.01 normal. Depth of cell, 10 cm. Starting with the lowest strip the temperatures are: 30°, 45°, 55°, 70°, and 80°.

B. Cobalt Bromide in Methyl Alcohol. Concentration, 0.01 normal. Depth of cell, 10 cm. Starting with the lowest strip the temperatures are: 34°, 44°, 55°, 66°, 81°, and 100°.

PLATE 51. *A*. Cobalt Bromide in Methyl Alcohol. Concentration, 0.1 normal. Depth of cell, 1.0 cm. Starting with the lowest strip the temperatures are: 31°, 46°, 58°, 64°, 68°, and 72°.

B. Cobalt Chloride in Methyl Alcohol. Concentration, 0.1 normal. Depth of cell, 1.0 cm. Starting with the lowest strip the temperatures are: 23°, 37°, 47°, 55°, 62°, 73°, and 93°.

PLATE 52. *A.* Neodymium Chloride in Water (8 per cent) and Ethyl Alcohol. Concentration, 0.3. Depth of cell, 1.0 cm. The exposures were started at 40° and ended at 80° C., the temperature being gradually increased in the interim.
B. Neodymium Chloride in Water and Alcohol. Concentration, 0.1 normal. Depth of cell, 1.0 cm. Range of temperature, starting from lowest strip, 20° to 85° C.

PLATE 53. *A.* Neodymium Chloride in Methyl Alcohol. Concentration, 0.2 normal. Depth of cell, 1.0 cm. Temperatures, 25°, 40°, 55°, and 70° C.
B. Uranous Chloride in Water. Range of temperature from 30° to about 80° C.
C. Neodymium Bromide in Water (8 per cent) and Methyl Alcohol. Concentration, 0.2 normal. Range of temperature, 30° to 80° C.

PLATE 54. *A.* Neodymium Chloride in Methyl Alcohol. Concentration, 0.1 normal. Depth of cell, 10 cm. Temperatures, 26°, 40°, 55°, 78°, and 85° C.
B. Neodymium Bromide in Methyl Alcohol. Concentration, 0.1 normal. Depth of cell, 10 cm. Temperatures, 25°, 35°, 44°, 60°, 82°, 100°, and 120° C. At the highest temperature a precipitate was formed.

PLATE 55. *A.* Neodymium Bromide in Water. Concentration, 1.66 normal. Depth of cell, 1.0 cm. Temperatures, 20°, 40°, 60°, 80°, and 93° C.
B. Neodymium Chloride in Water. Concentration, 2.05 normal. Depth of cell, 1.0 cm. Temperatures, 20°, 50°, and 75° C.
Neodymium Nitrate in Water. Concentration, 2.15 normal. Depth of cell, 1.0 cm. Temperatures, 20°, 75°, and 95° C.

PLATE 56. *A.* Neodymium Chloride in Acetone, 10° and 70° C.
Neodymium Chloride in Ether, 10° C.
Neodymium Chloride in Ethyl Alcohol, 10° and 70° C.
Neodymium Chloride in Ethyl Alcohol and Hydrochloric Acid at 10° and 70° C.
B. Neodymium Nitrate in Nitric Acid, 10° and 50° C.
Neodymium Chloride in Water (8 per cent) and Methyl Alcohol at 10° and 70° C.
Neodymium Nitrate in Water (8 per cent) and Acetone at 10° and 60° C.
Neodymium Chloride in Water (40 per cent) and Ethyl Alcohol at 10° C.
Neodymium Chloride in Water (40 per cent) and Glycerol at 10° C.

PLATE 57. *A.* Neodymium Nitrate in Water and Methyl Alcohol. Concentration, 0.25 normal. The variable here is the percentage of water.
B. Neodymium Bromide in Water (8 per cent) and Methyl Alcohol. Concentration, 0.2 normal. Depth of cell, 1.0 cm. Temperature range, 25° to 115° C.

PLATE 58. *A.* Neodymium Nitrate in Water (14 per cent) and Methyl Alcohol. Concentration, 0.3 normal. Depth of cell, 1.0 cm. Temperature range, 25° to 115° C.
B. Neodymium Bromide in Water (8 per cent) and Ethyl Alcohol. Concentration, 0.2 normal. Depth of cell, 1.0 cm. Temperature range, 25° to 87° C.

PLATE 59. *A.* Neodymium Chloride in Water at 10° and 90° C.
Neodymium Chloride in Hydrochloric Acid at 10° and 90° C.
Neodymium Chloride in Methyl Alcohol.
Neodymium Chloride and Sodium Chlorate in Methyl Alcohol.
B. Neodymium Acetate in Water at 10° and 90° C.
Neodymium Chloride in Acetic Acid at 10° and 90° C.
Neodymium Acetate in Acetic Acid at 10° and 90° C.
Neodymium Acetate in Methyl Ester and Acetic Acid at 10° and 90° C.

PLATE 60. *A.* Erbium Chloride in Water at 20°, 30°, 85°, and 115° C.
B. Neodymium Chloride in Water. Concentration, 0.2 normal. Depth of cell, 10 cm. Temperatures, 20°, 50°, 85°, and 115° C.
C. Neodymium Nitrate in Tertiary Butyl Alcohol. Concentration, 0.2 normal. Depth of cell, 1.0 cm. Temperatures, 25°, 50°, and 65° C.
Neodymium Nitrate in Isobutyl Alcohol at 20°, 75°, and 100° C.

PLATE 61. *A*. Uranyl Chloride in Isobutyl Alcohol. Concentration, 0.005 normal. Depth of cell, 10 cm. Temperatures, 18°, 40°, 60°, 80°, 100°, and 90° C.

B. Erbium Chloride in Methyl Alcohol. Depth of cell, 10 cm. Temperatures, 20°, 45°, 75°, 110°, 125°, and 165° (after a precipitate had been formed).

PLATE 62. *A*. Uranyl Chloride in Isobutyl Alcohol. Concentration, 0.076 normal. Depth of cell, 10 cm. Temperatures, 20°, 60°, 85°, and 115° C.

B. Uranyl Nitrate in Isobutyl Alcohol. Concentration, 0.033 normal. Depth of cell, 10 cm. Temperatures, 20°, 50°, 80°, 100°, and 115° C.

PLATE 63. *A*. Uranyl Nitrate in Methyl Alcohol. Concentration, 0.2 normal. Depth of cell, 1.0 cm. Temperatures, 20°, 100°, 135°, 145° (precipitate), and 160° C.

B. Uranyl and Calcium Chlorides in Methyl Ester at 20°, 45°, and 85° C.
Uranyl and Calcium Chlorides in Methyl Alcohol at 20°, 50°, and 95° C.

PLATE 64. *A*. Uranyl Chloride in Methyl Ester. Concentration, 0.005 normal. Depth of cell, 10 cm. Temperatures, 20°, 45°, 70°, 90°, 110°, 135°, and 140° C.

B. Uranyl Nitrate in Propyl Alcohol. Concentration, 0.005 normal. Depth of cell, 10 cm. Temperatures, 20°, 40°, 65°, 85°, 105°, 115°, 130°, and 145° C.

PLATE 65. *A*. Uranyl Chloride in Propyl Alcohol. Concentration, 0.01 normal. Depth of cell, 10 cm. Temperatures, 22°, 45°, 70°, 90°, and 100° C.

B. Uranyl Chloride in Methyl Alcohol. Concentration, 0.005 normal. Depth of cell, 10 cm. Temperatures. 20°, 45°, 65°, 85°, 110°, 120°, and 145° C.

PLATE 66. *A*. Uranyl Chloride in Methyl Ester. Concentration, 0.034 normal. Uranous Chloride in Methyl Ester (strips 2 and 3); Uranyl Nitrate in Methyl Ester; Uranyl Chloride in Methyl Alcohol; and Uranyl Nitrate in Methyl Alcohol.

B. Uranyl Nitrate in Methyl Ester. Concentration, 0.005 normal. Depth of cell, 10 cm. Temperatures, 20°, 50°, 75°, 100°, 125°, and 145° C.

PLATE 67. *A*. Uranous Sulphate in Sulphuric Acid at 10° and 90° C.
Uranous Sulphate in Water at 10° and 90° C.
Uranous Chloride in Water and Methyl Alcohol at 10° and 70° C.

B. Uranyl Nitrate in Nitric Acid at 10° and 70° C.
Uranyl Chloride in Hydrochloric Acid at 10° and 80° C.
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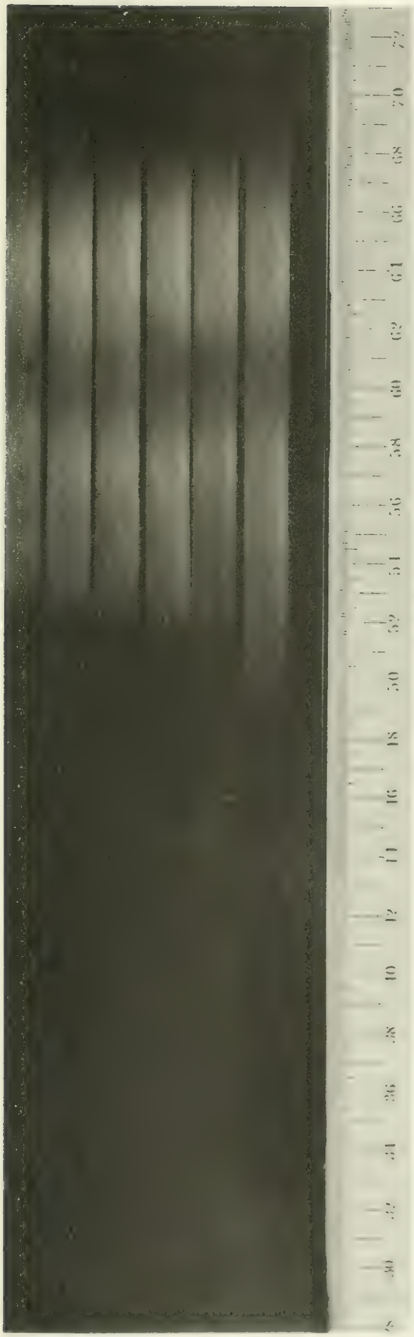

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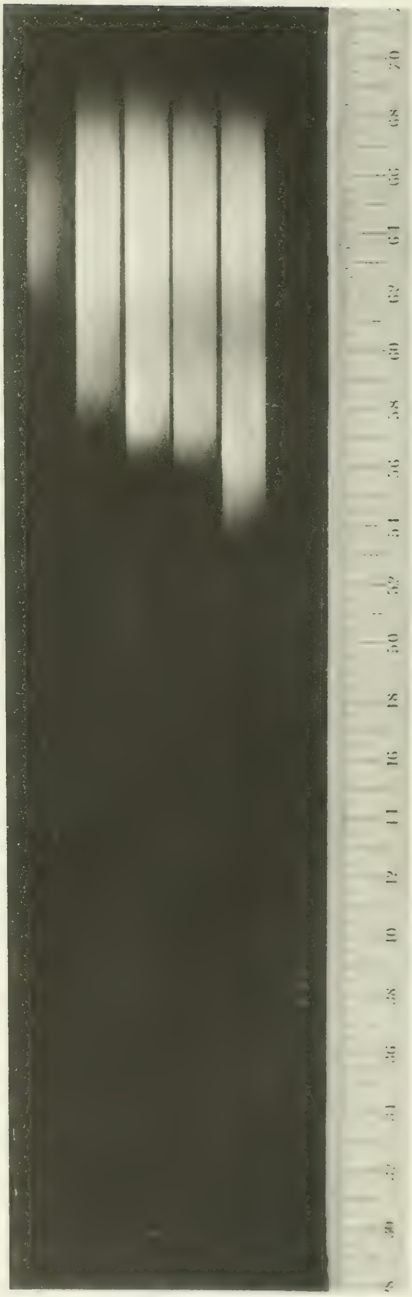

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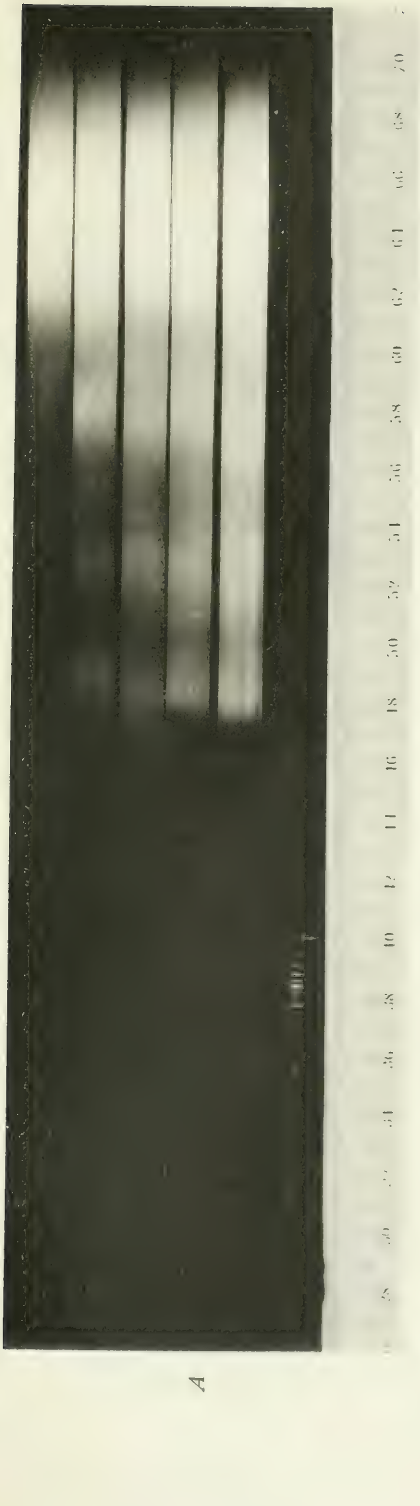
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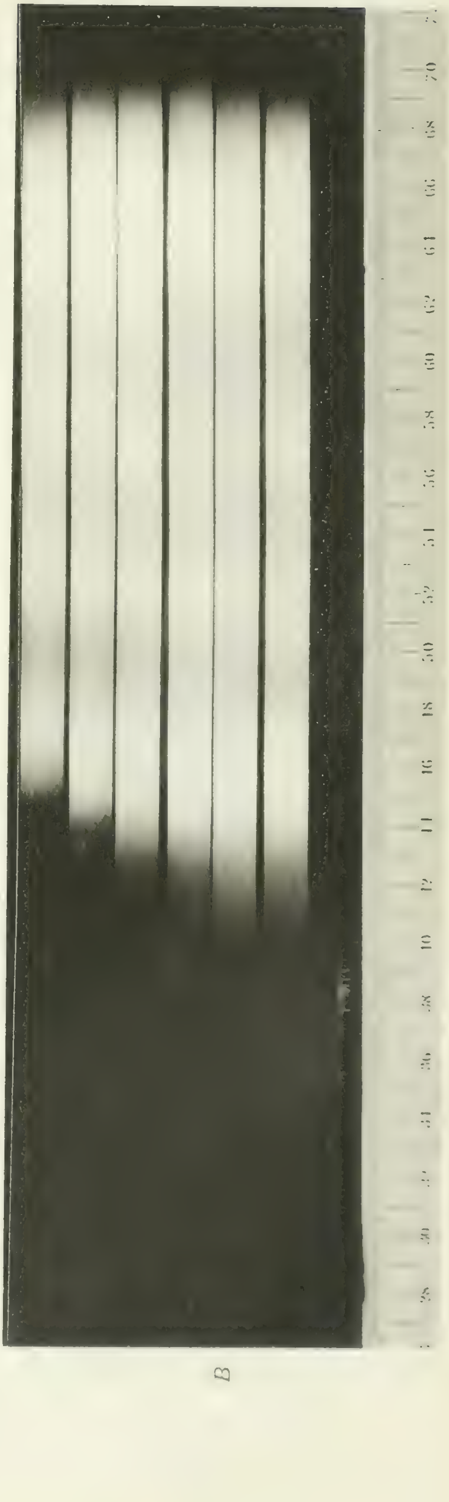
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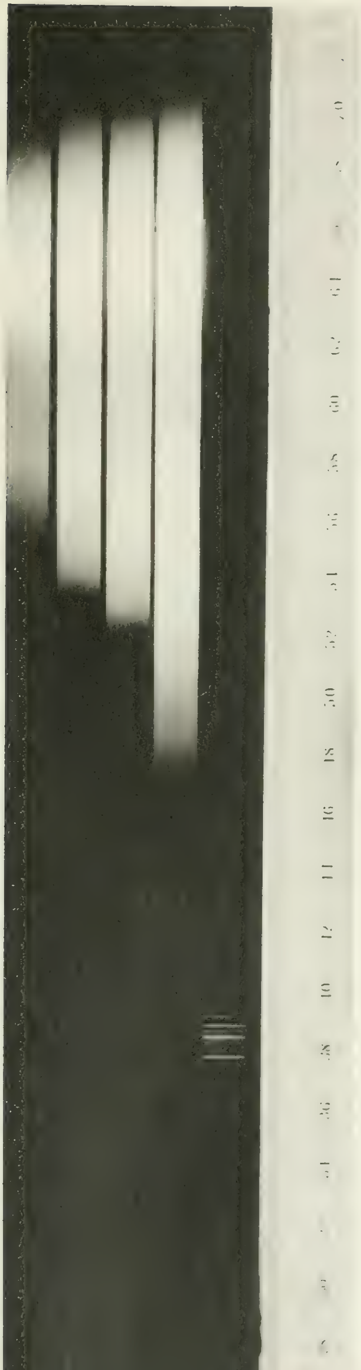

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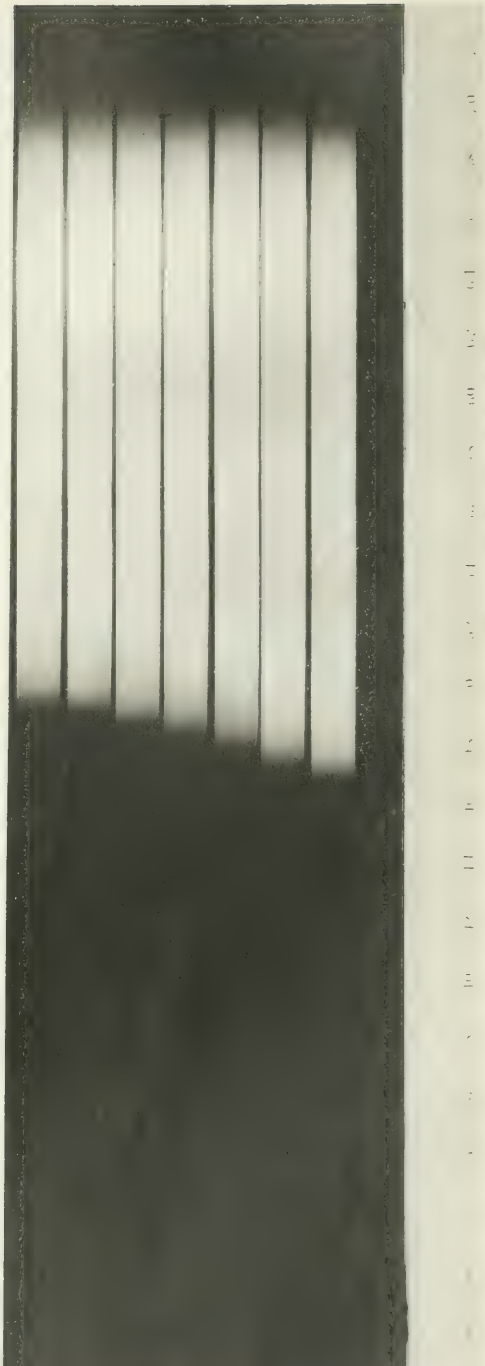

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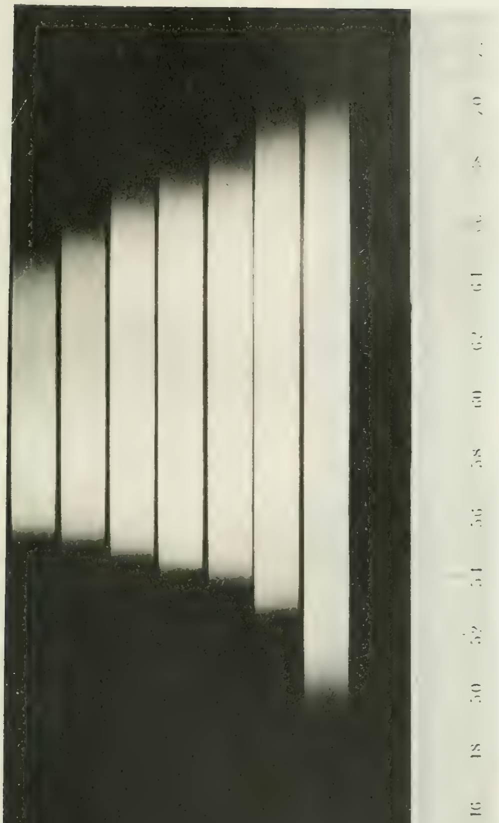

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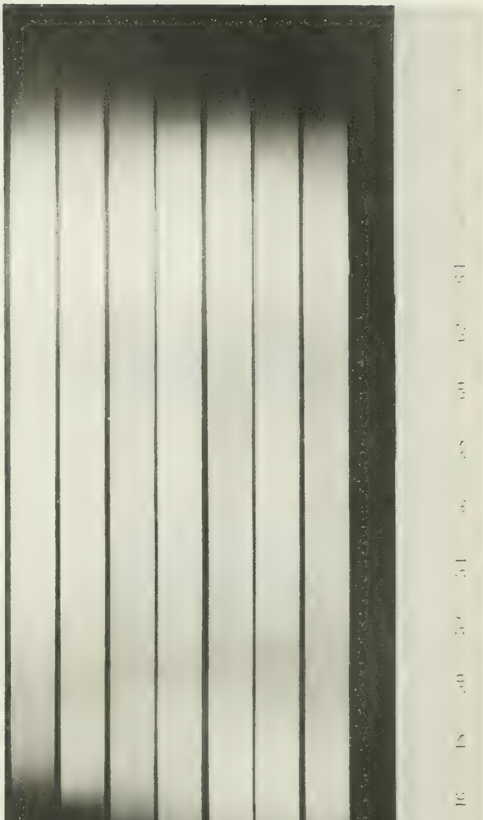

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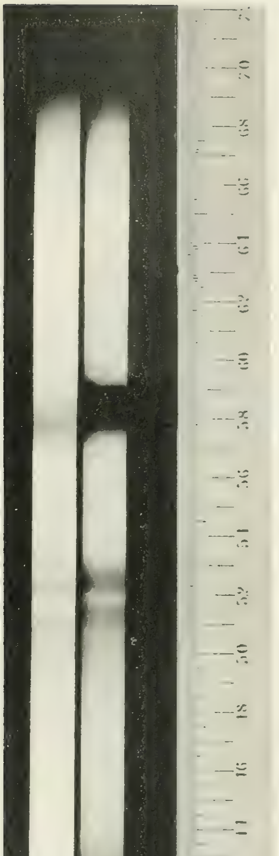

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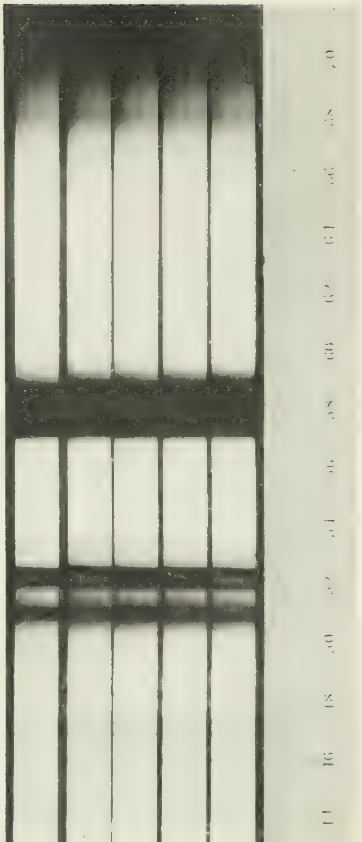

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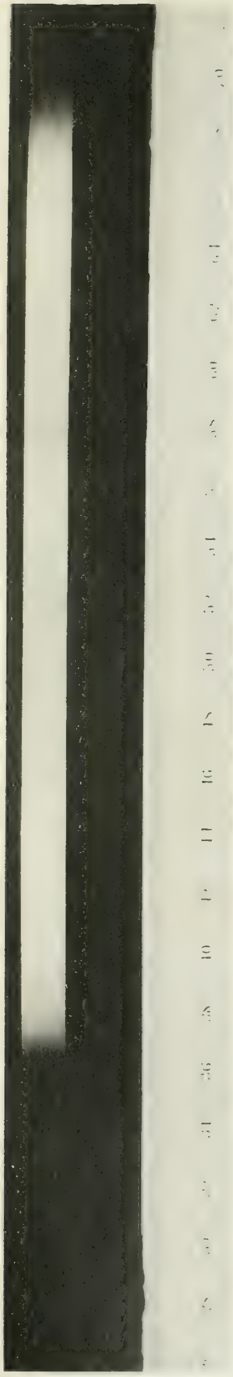

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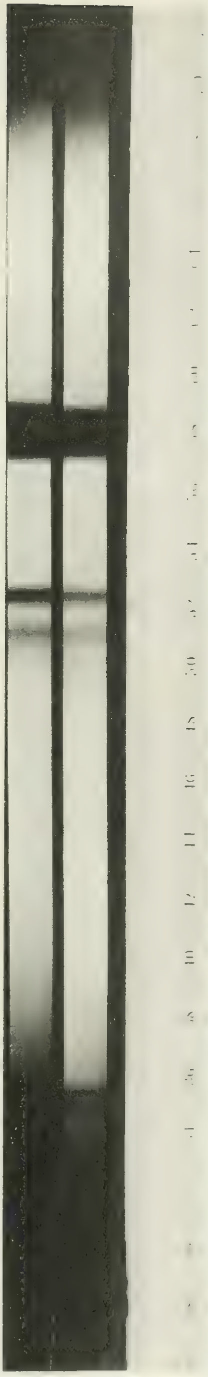

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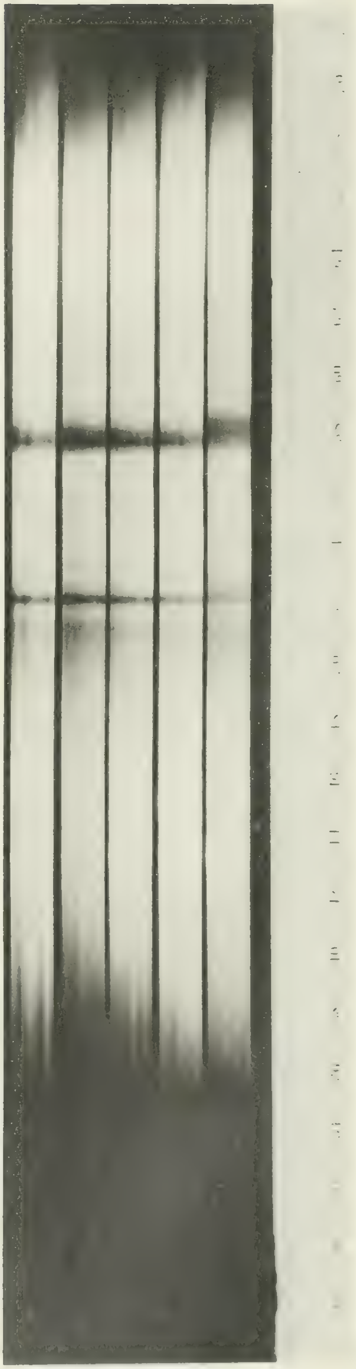

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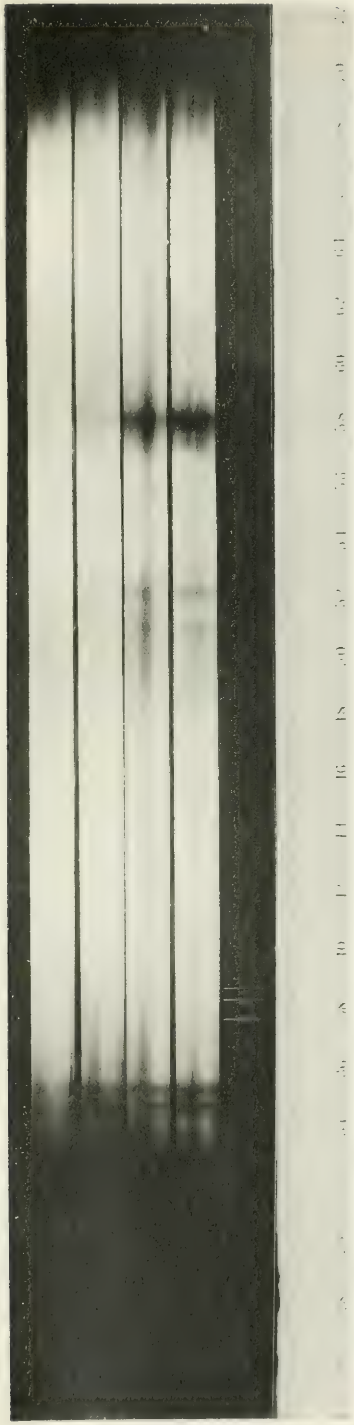

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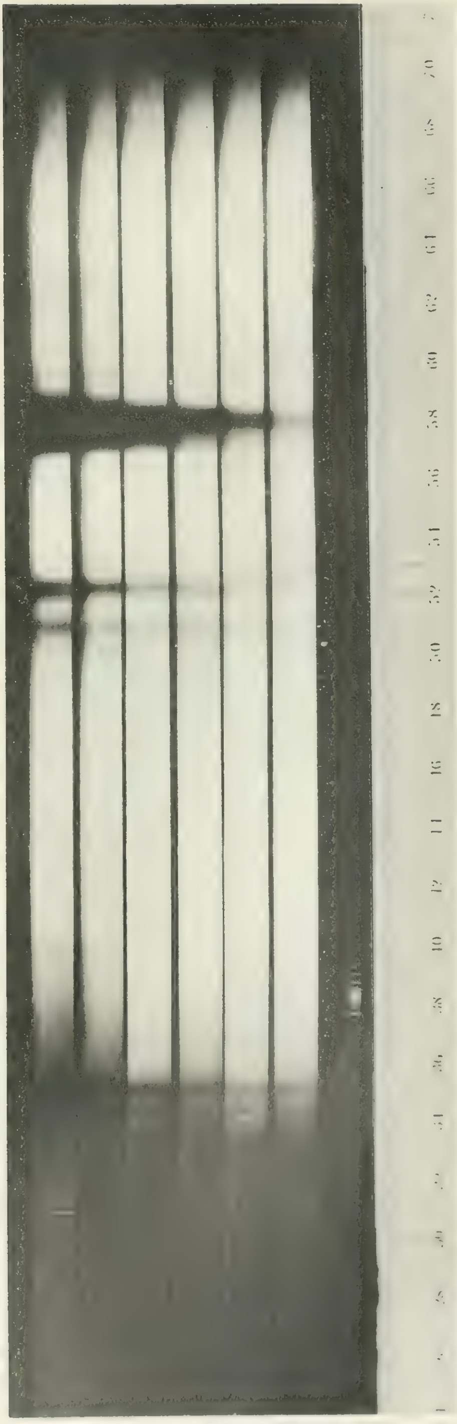

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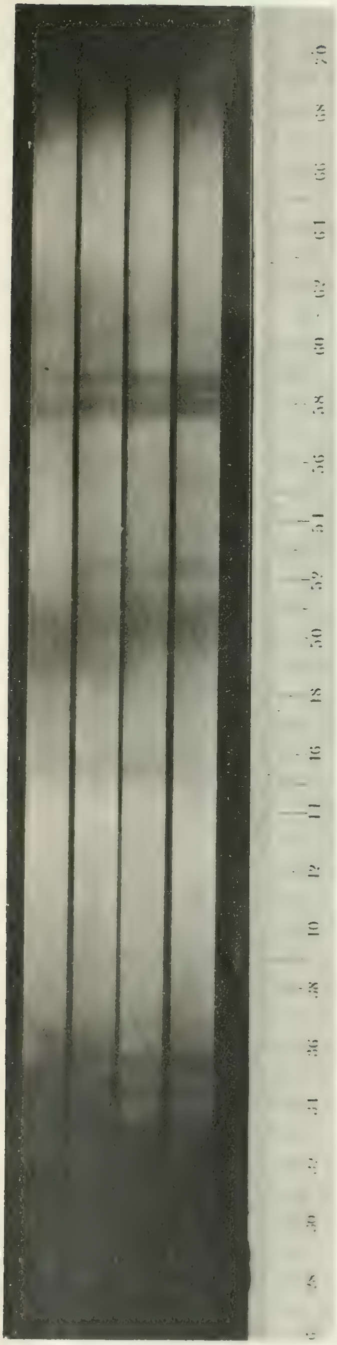
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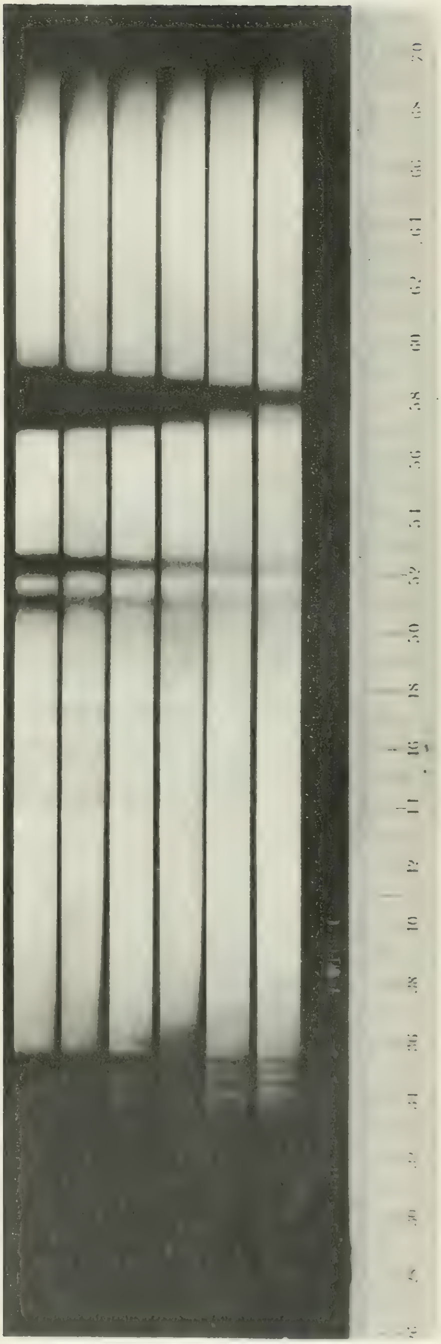
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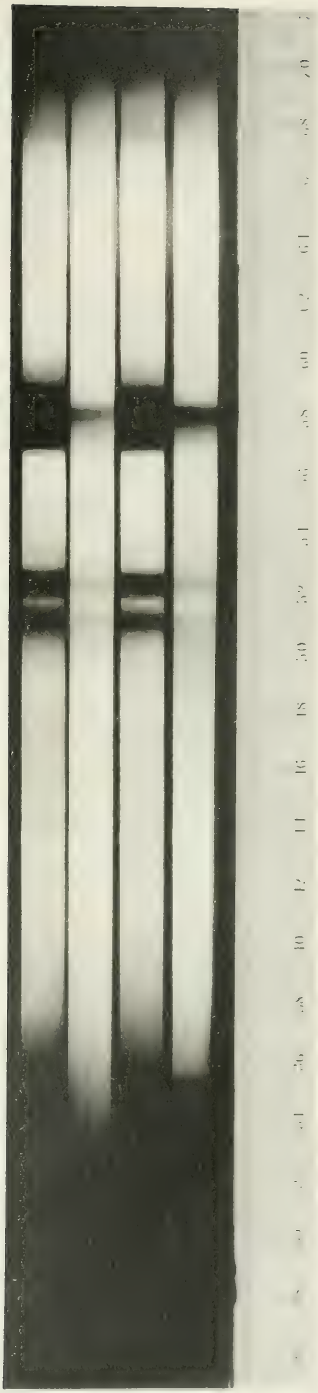
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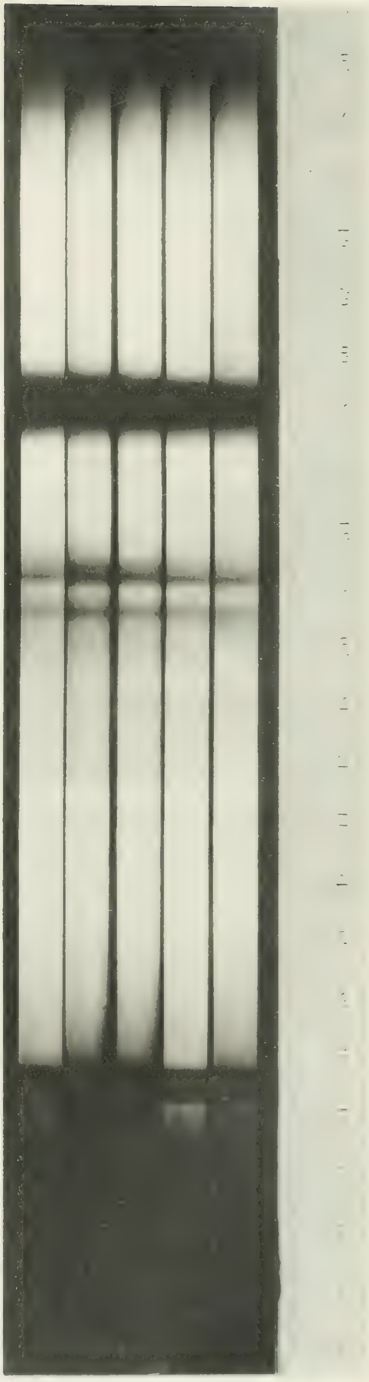
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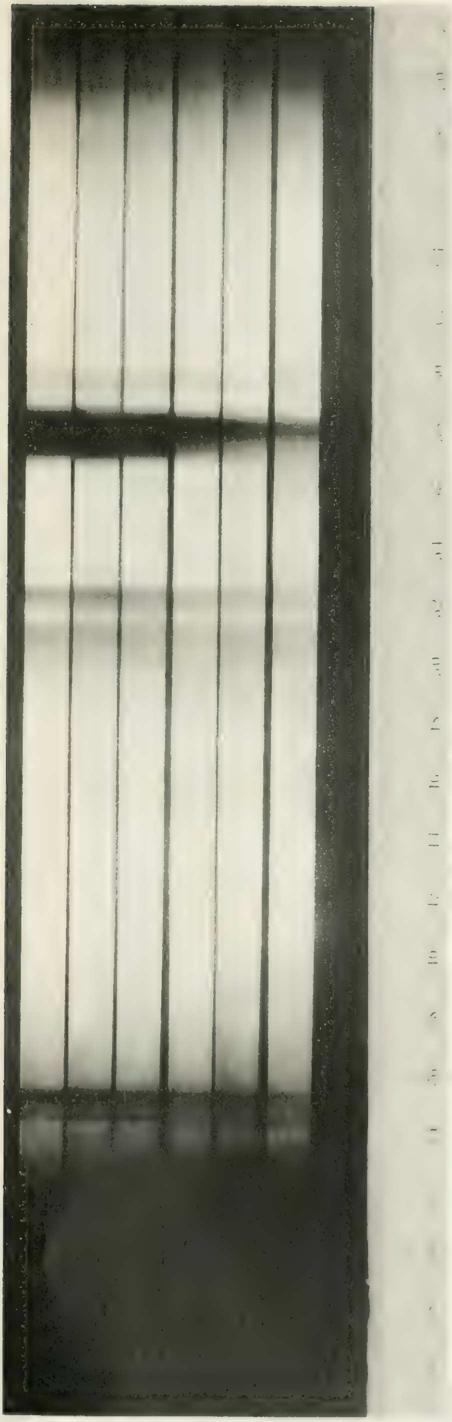

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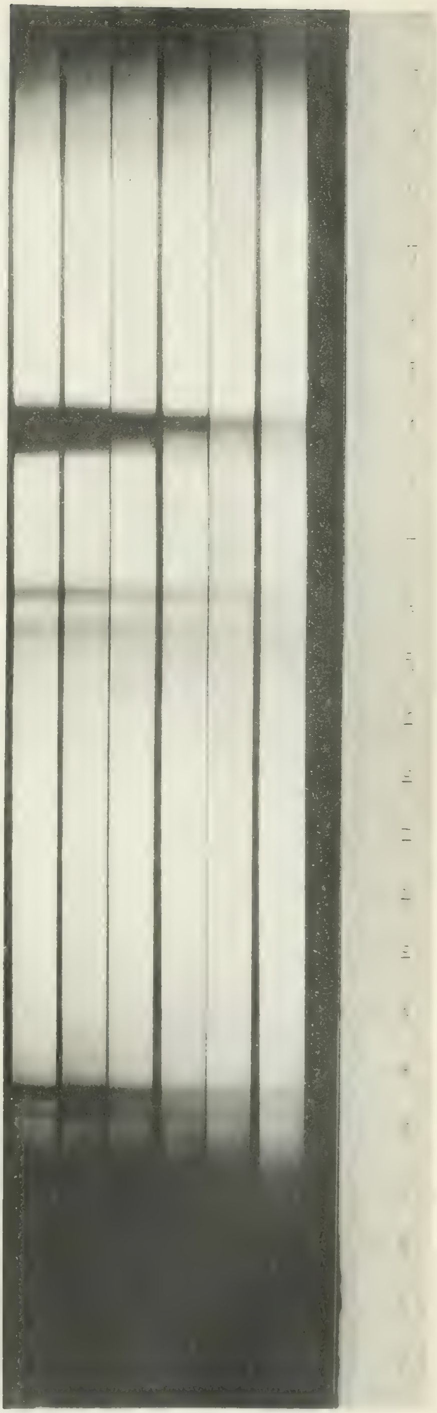

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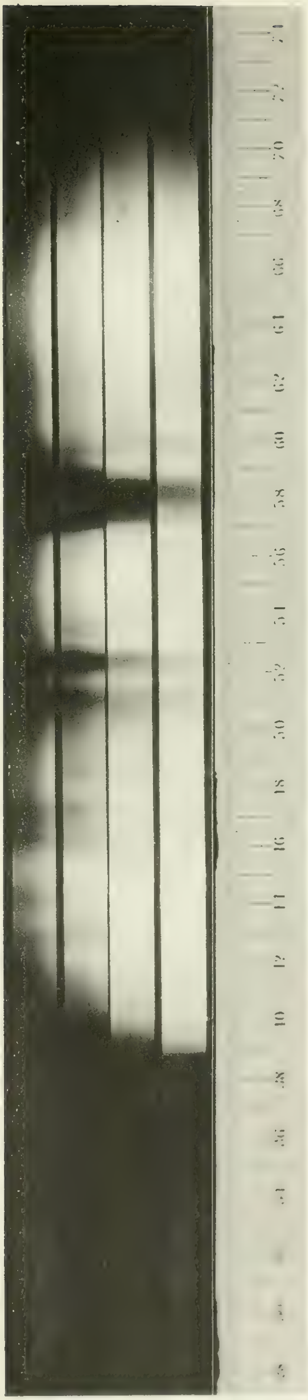

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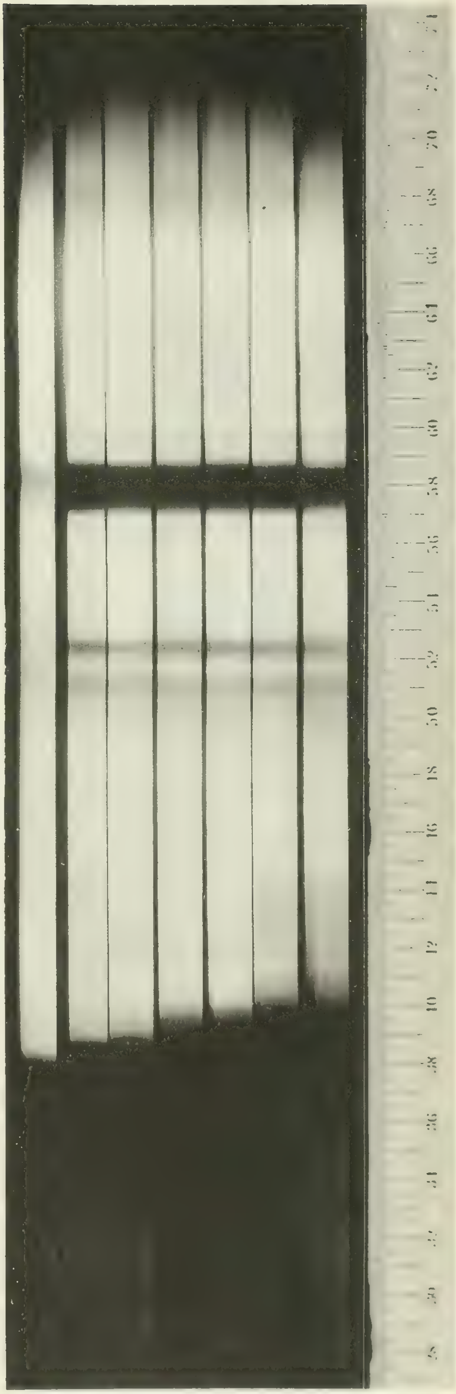

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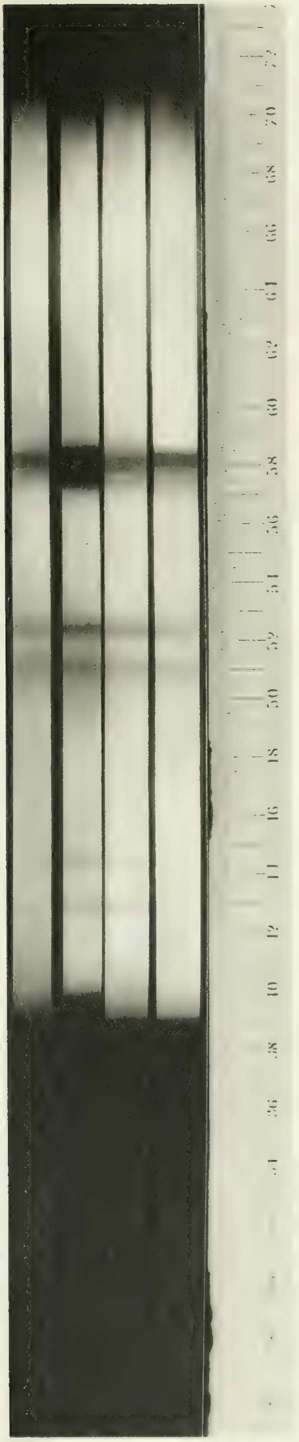

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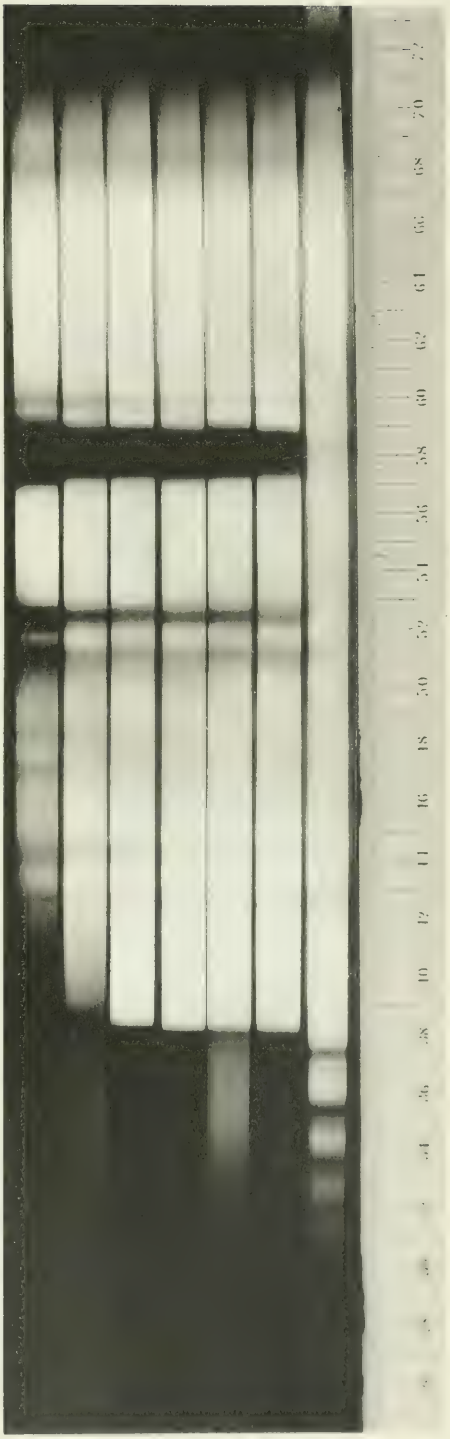

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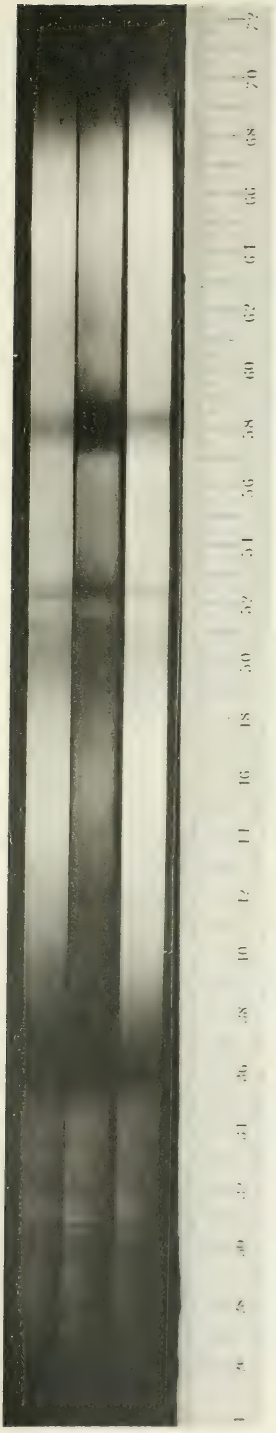

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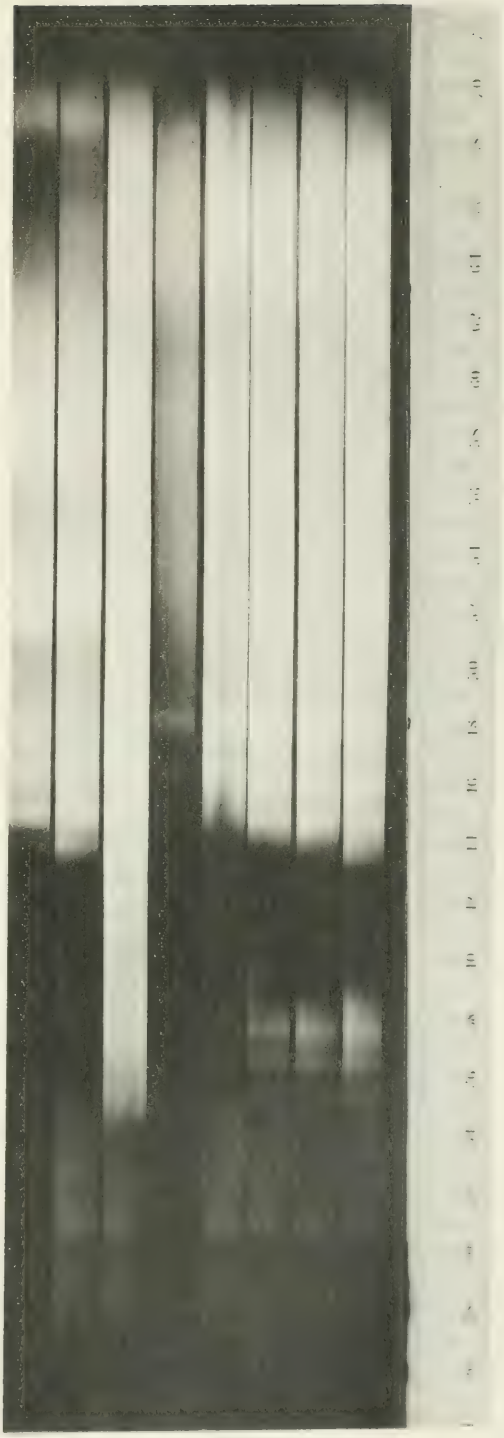

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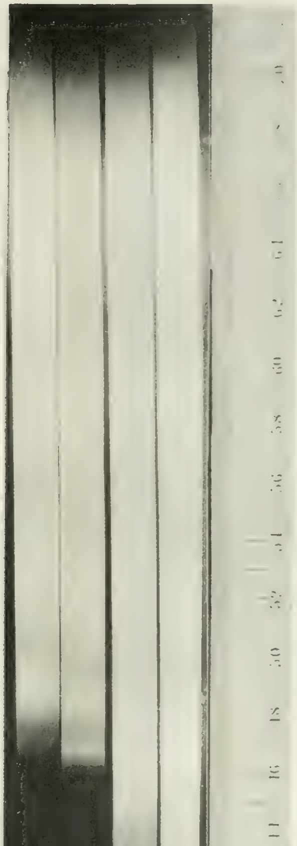

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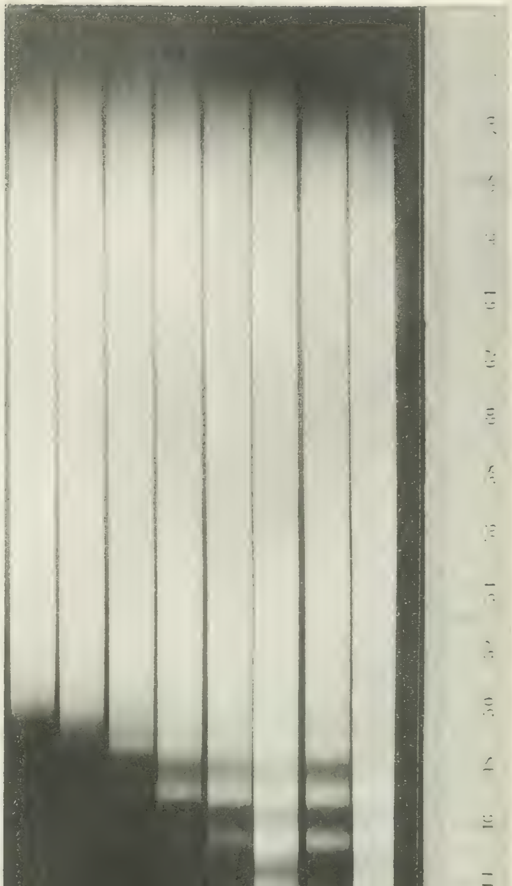

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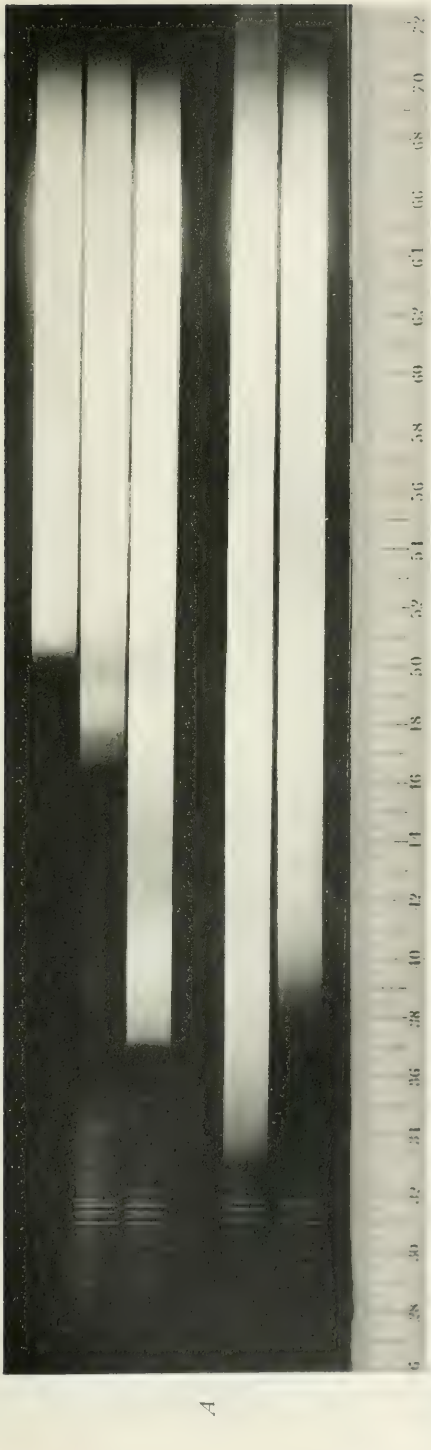
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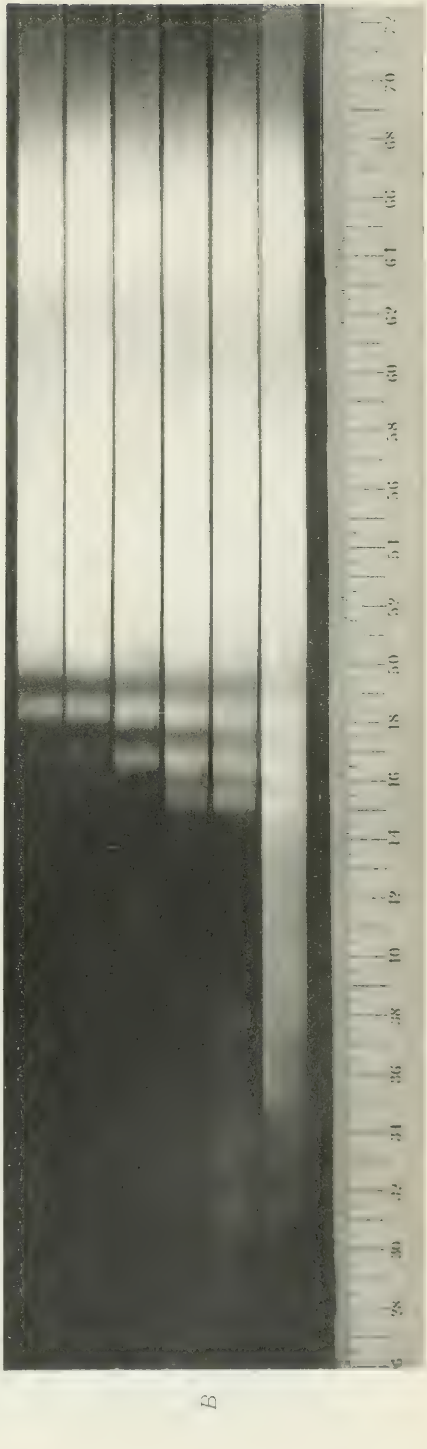
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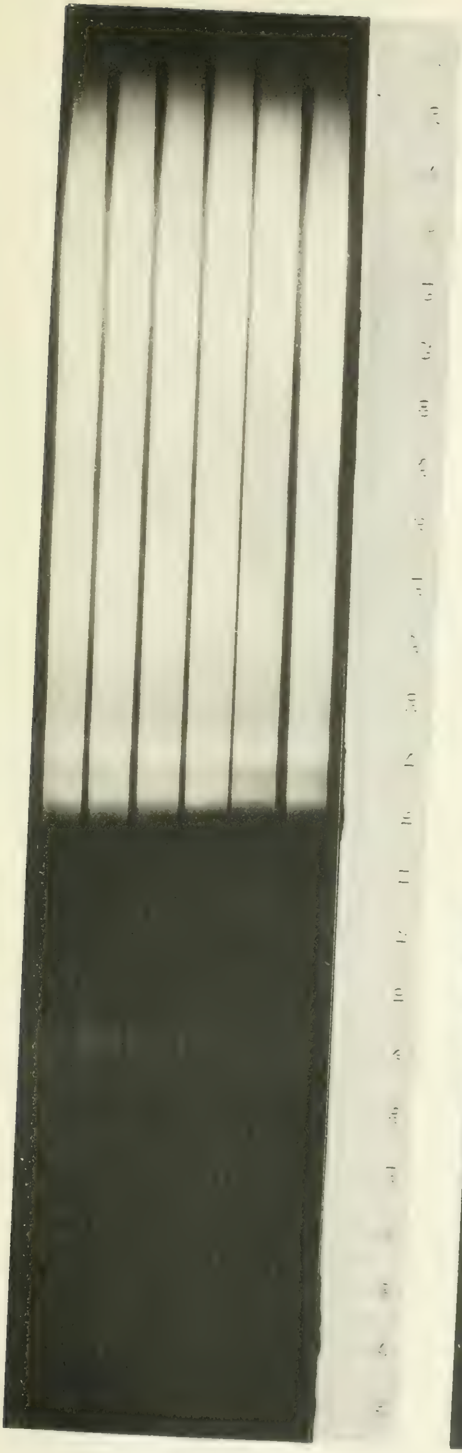

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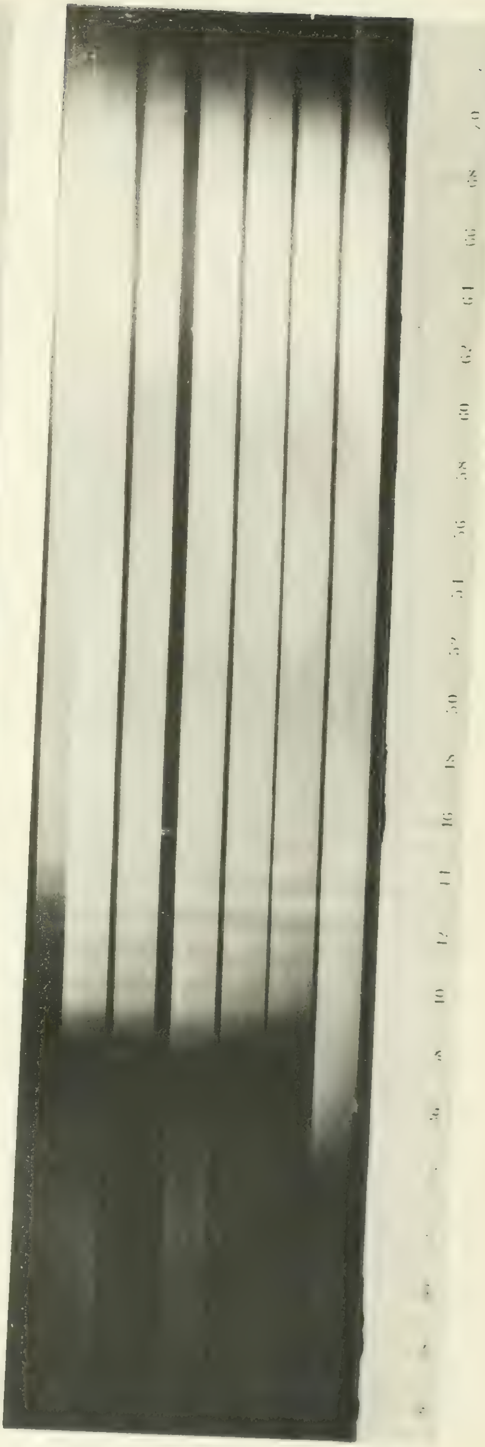

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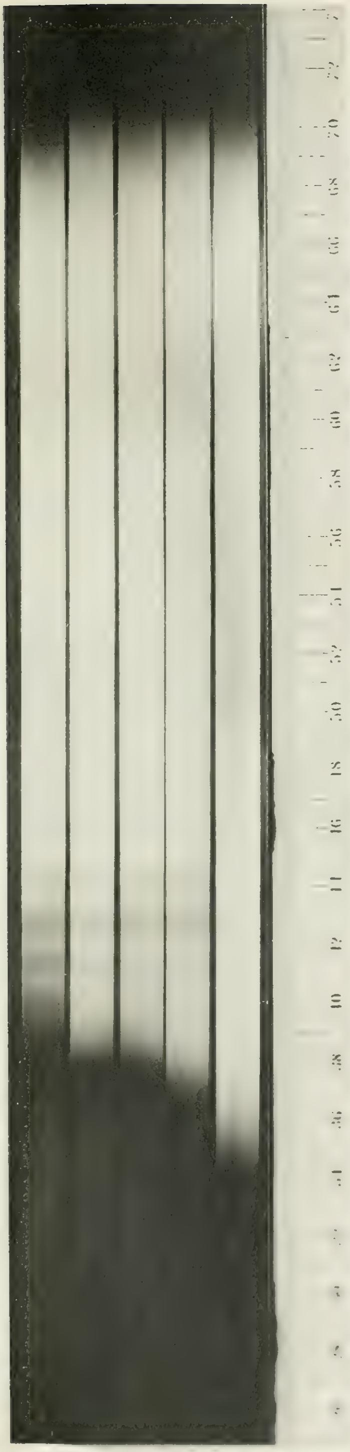

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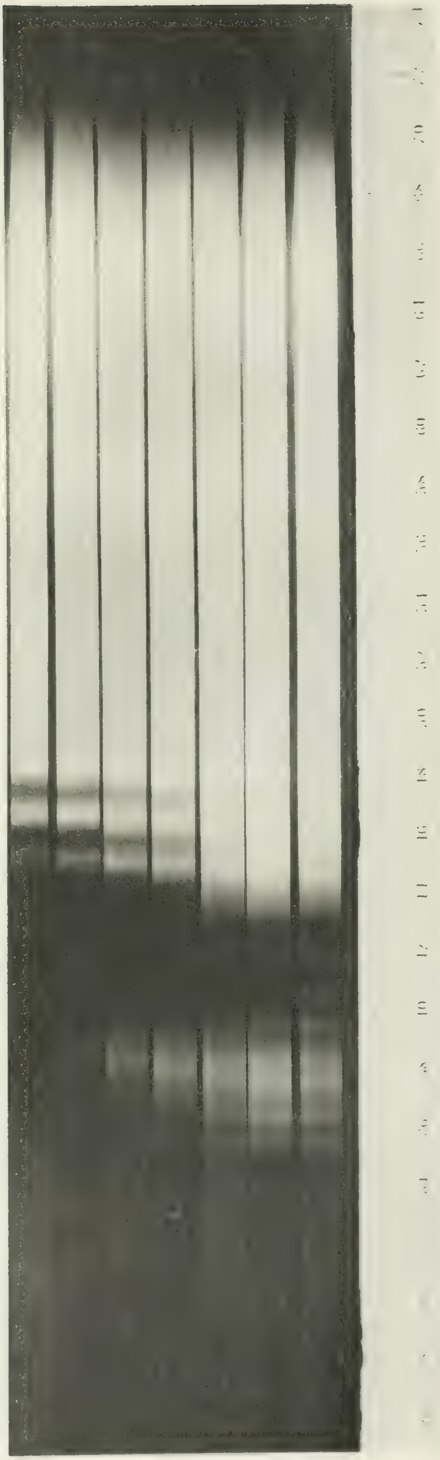

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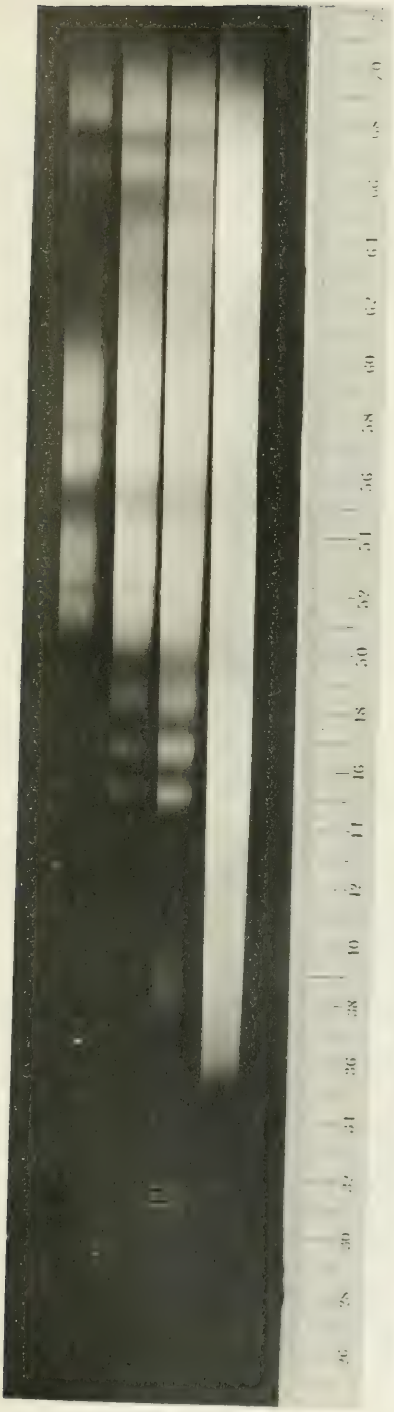
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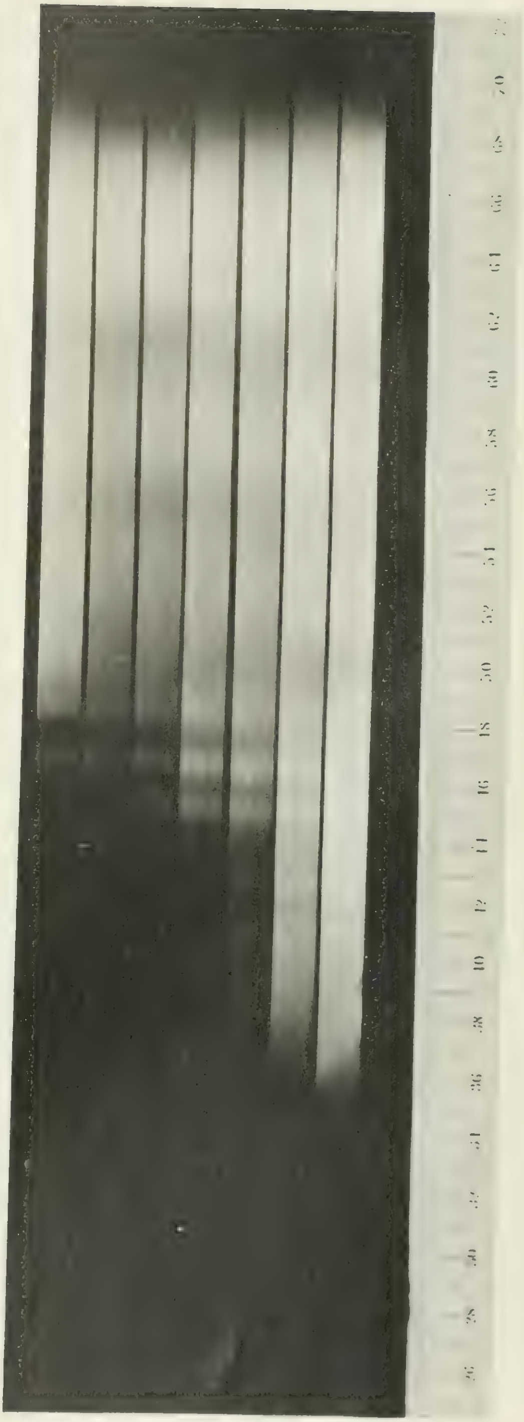
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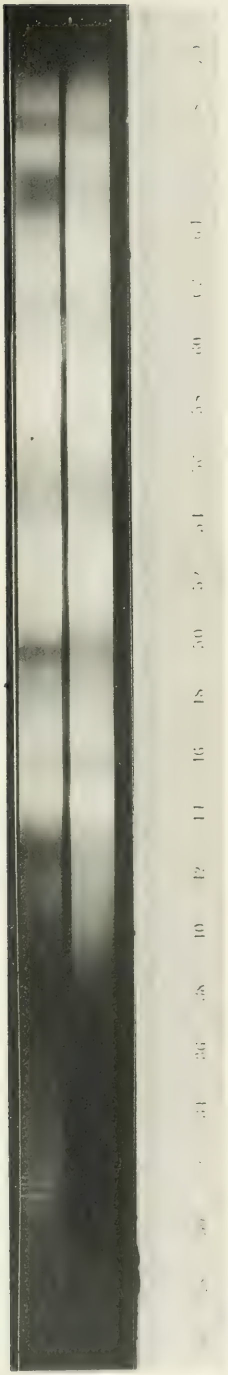

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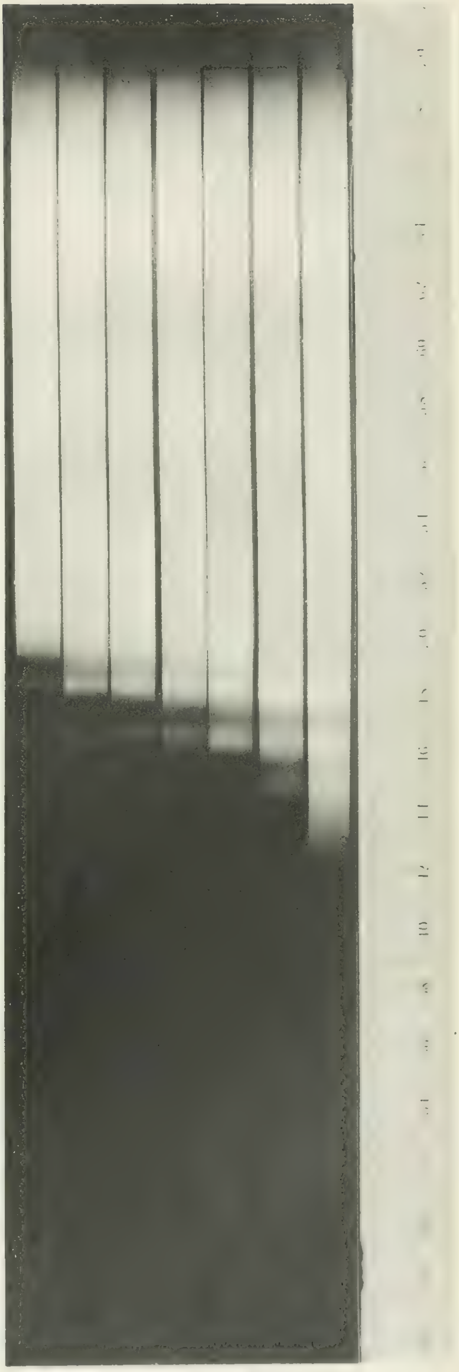

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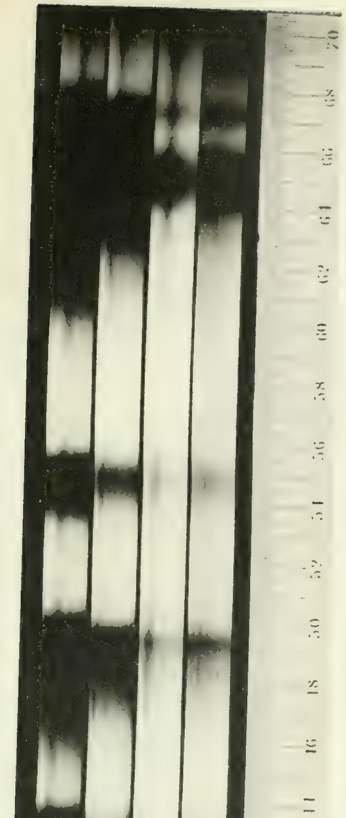
CAMPBELL ART CO., ELIZABETH, N. J.



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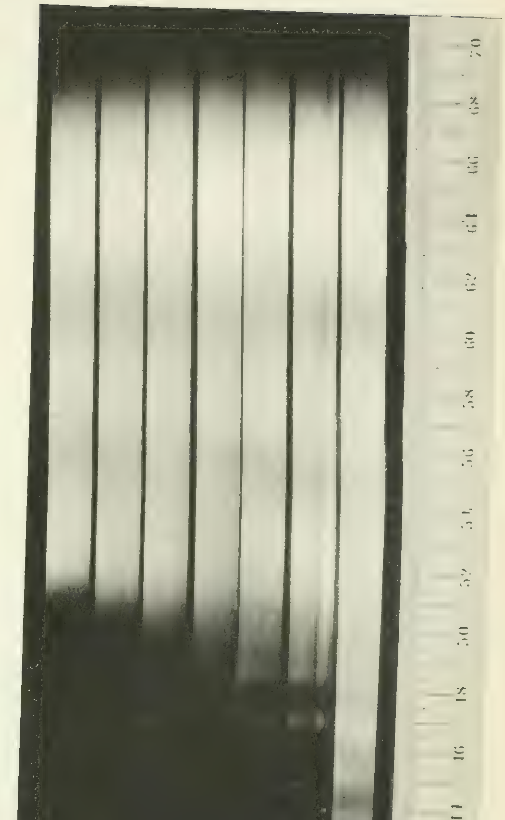

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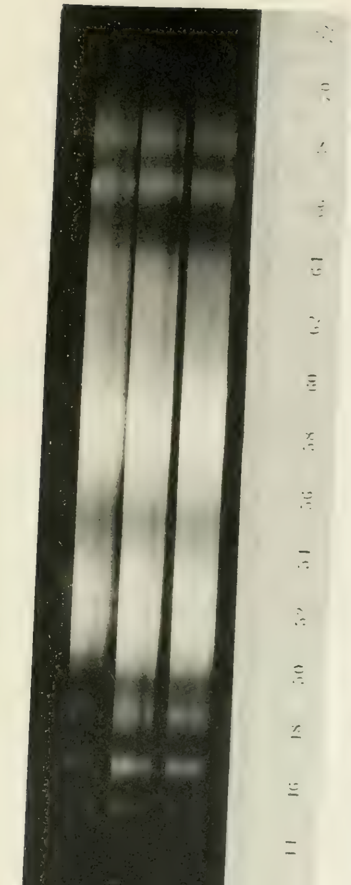
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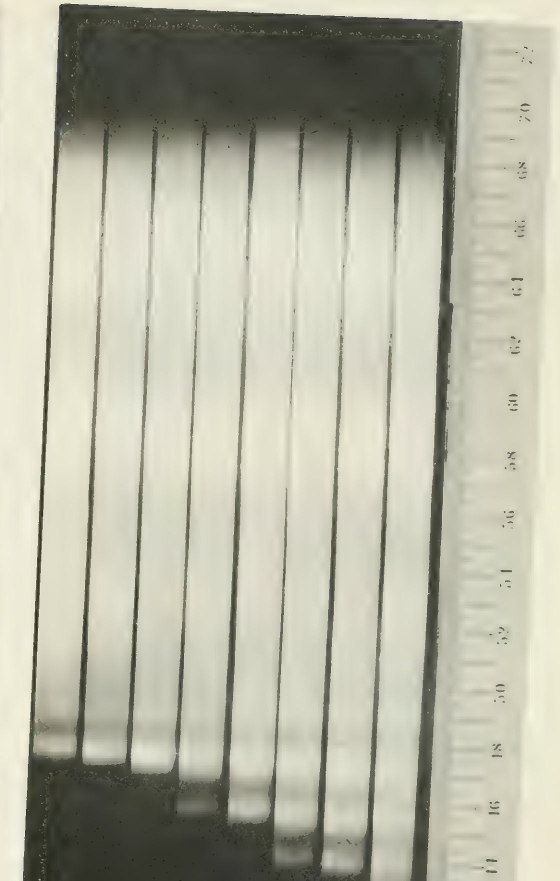
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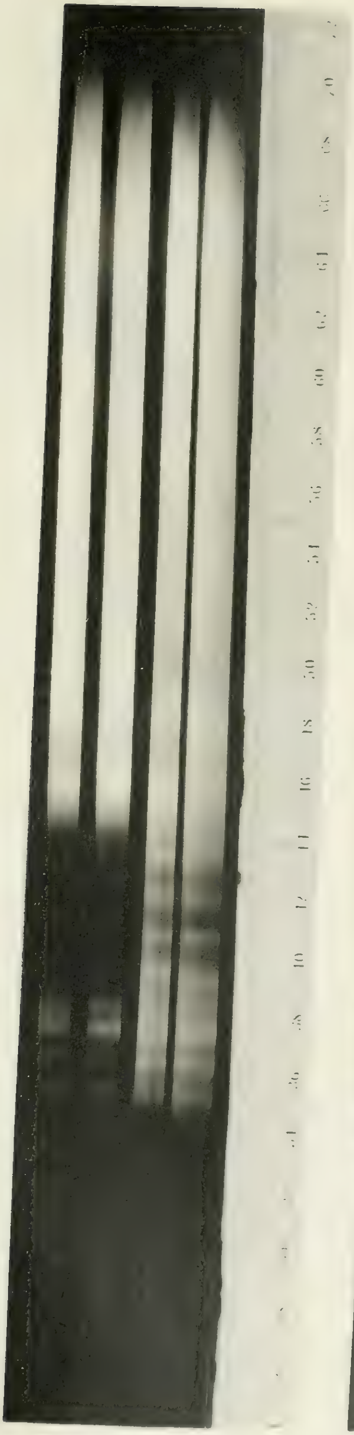
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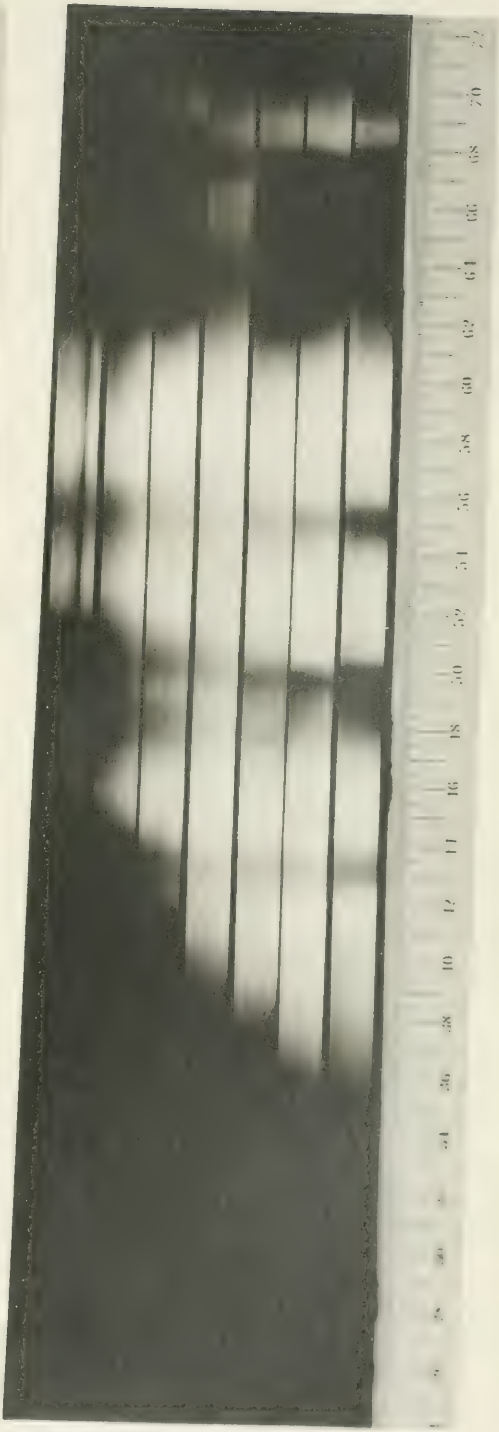
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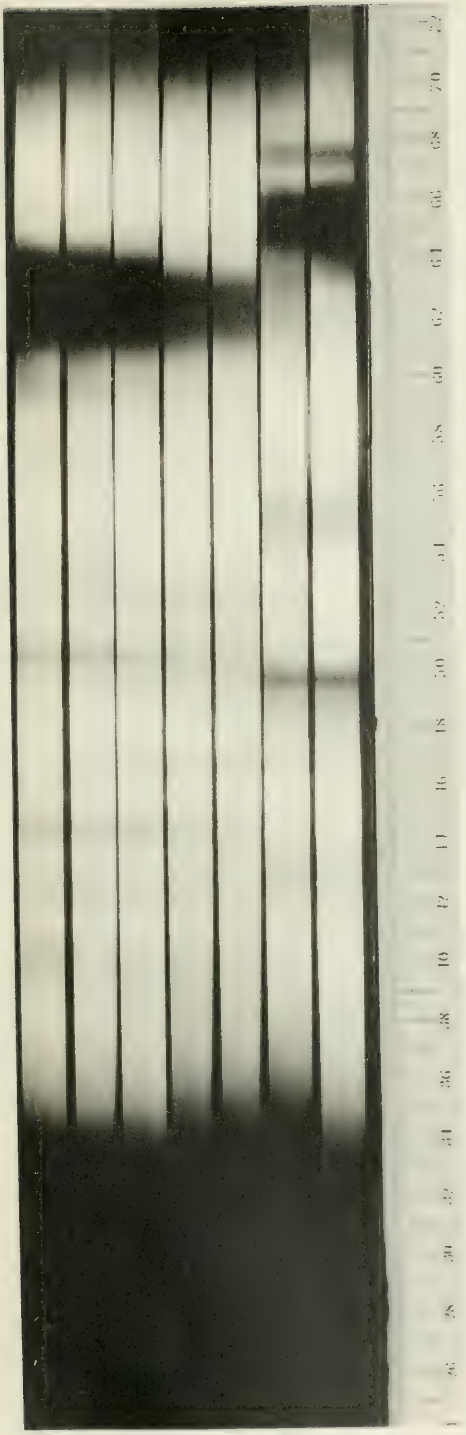
CAMERA ART CO. ELIZABETH, N. J.



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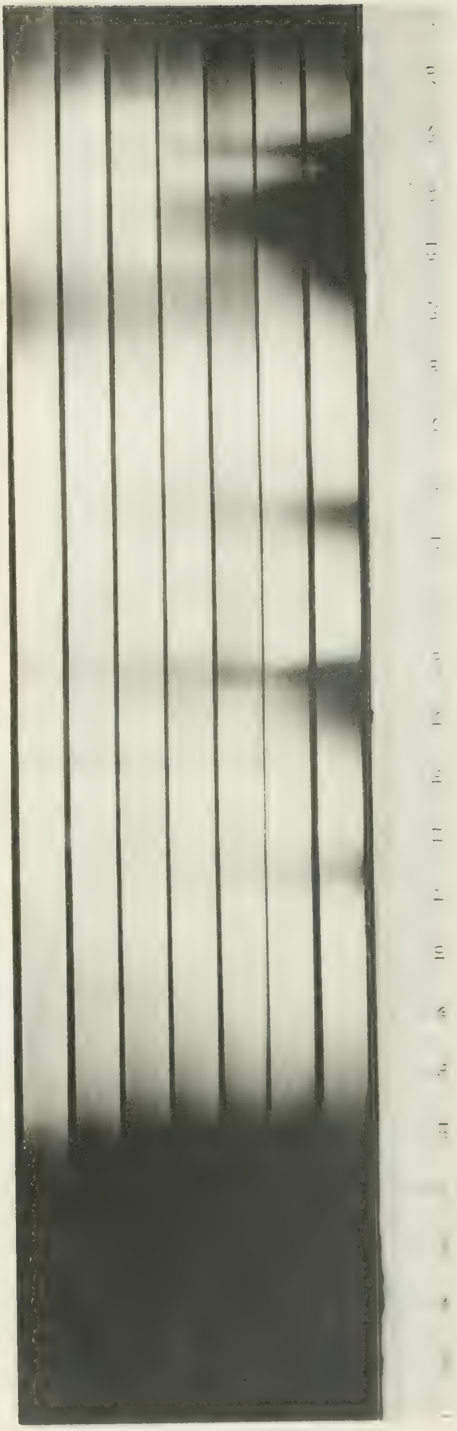

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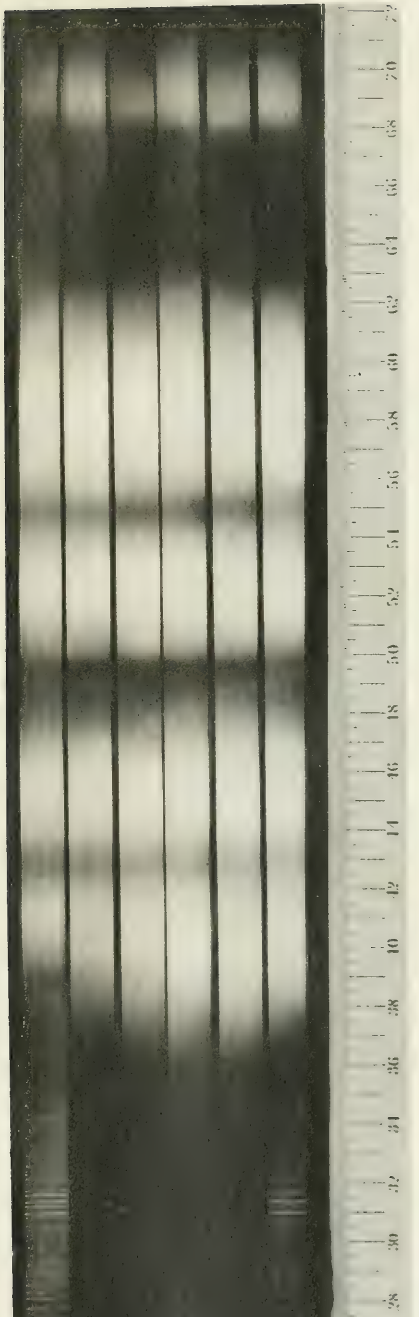
CAMPBELL ART CO., ELIZABETH, N. J.

PLATE 24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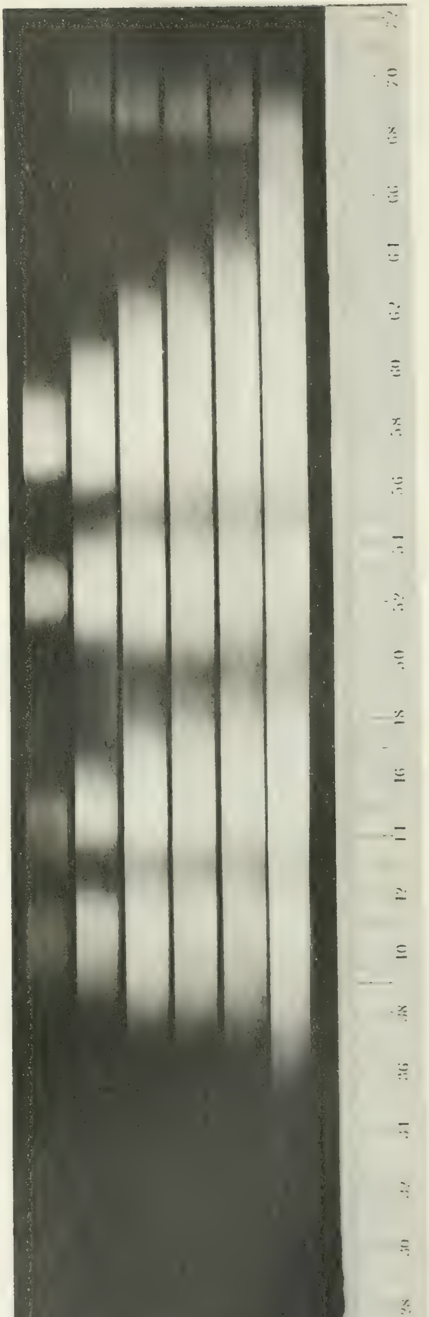
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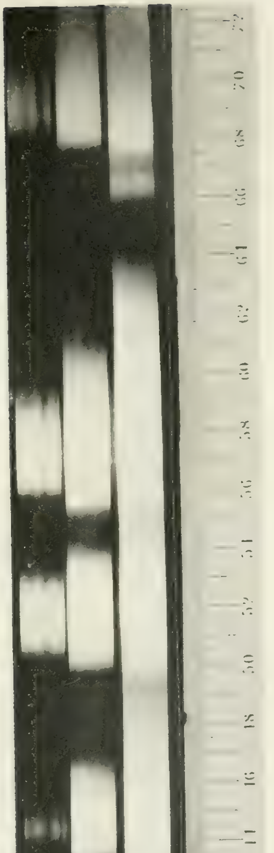
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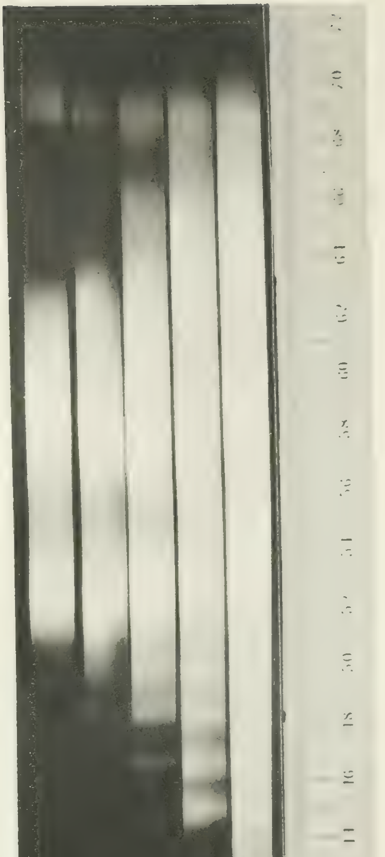
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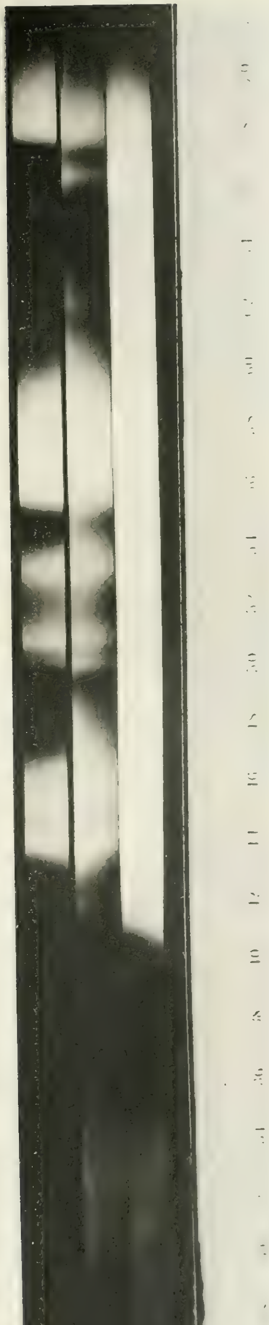

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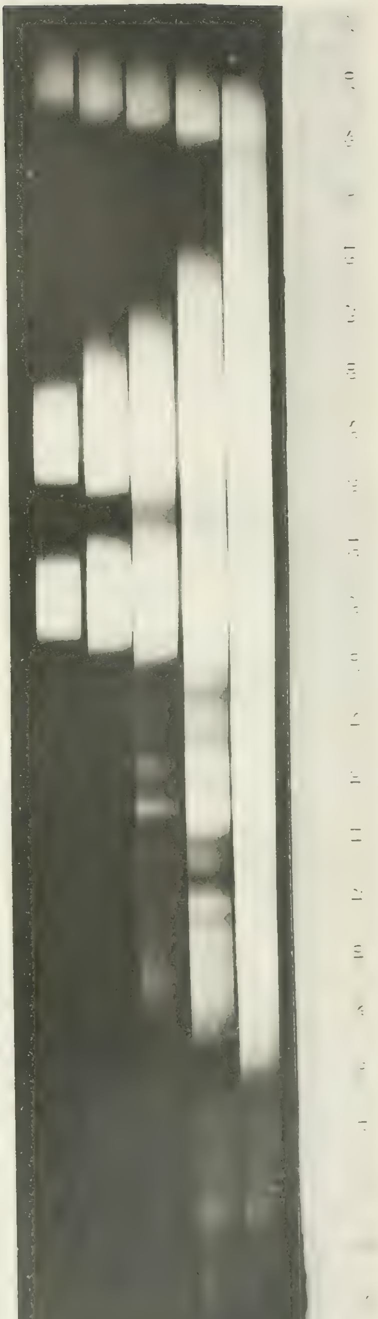

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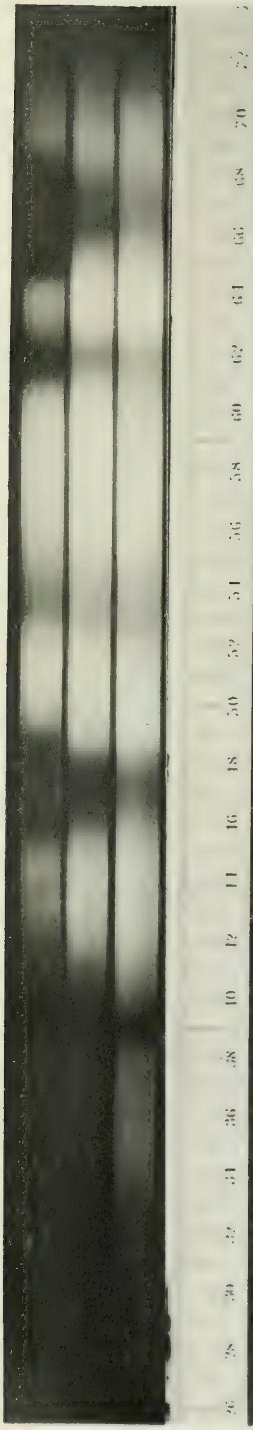
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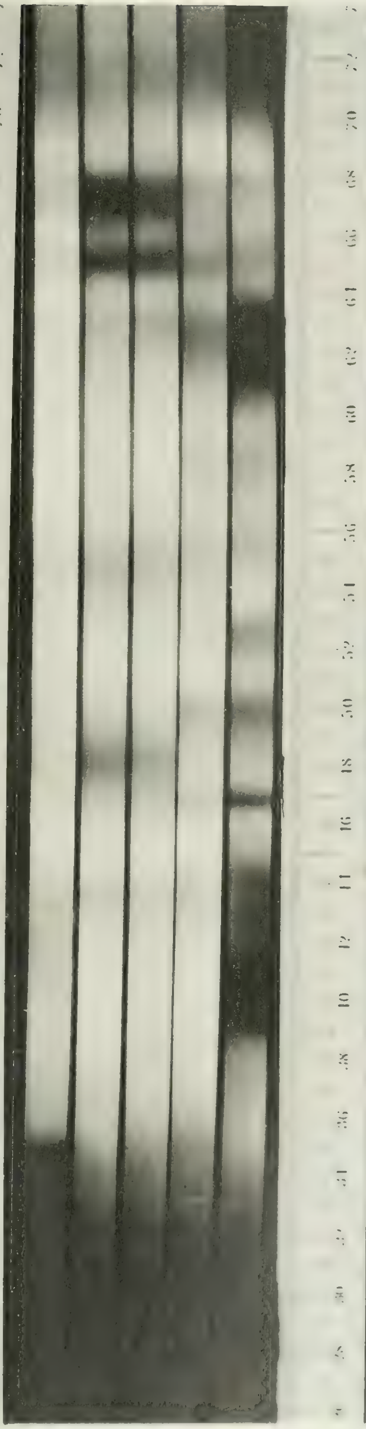
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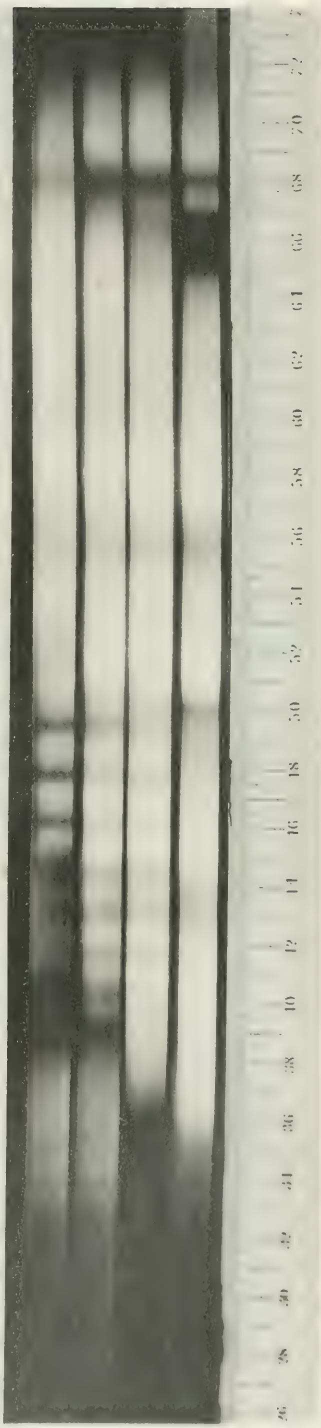
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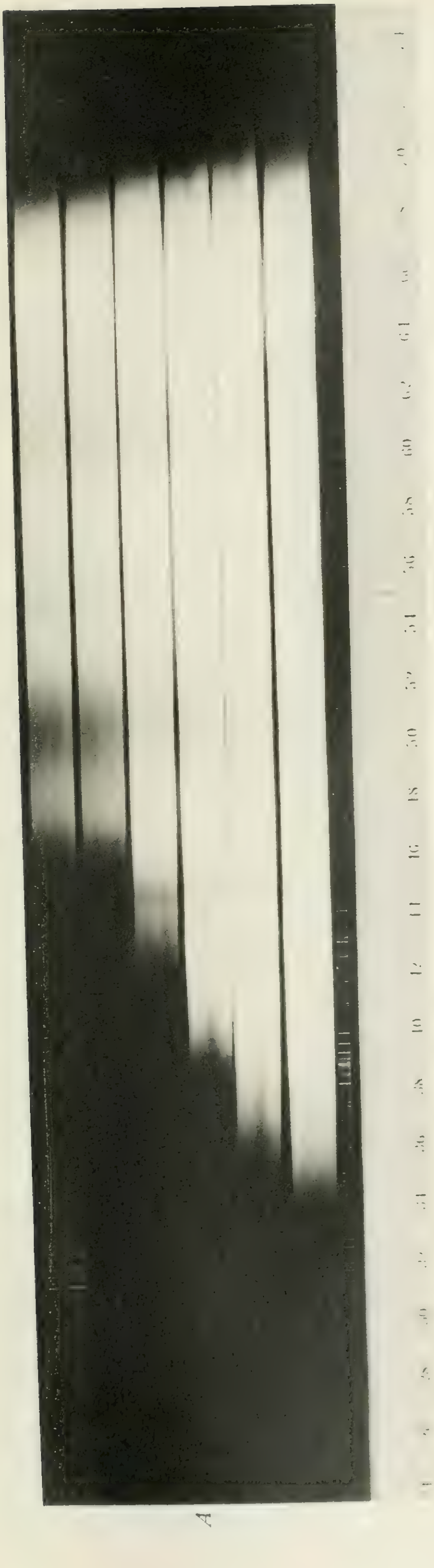

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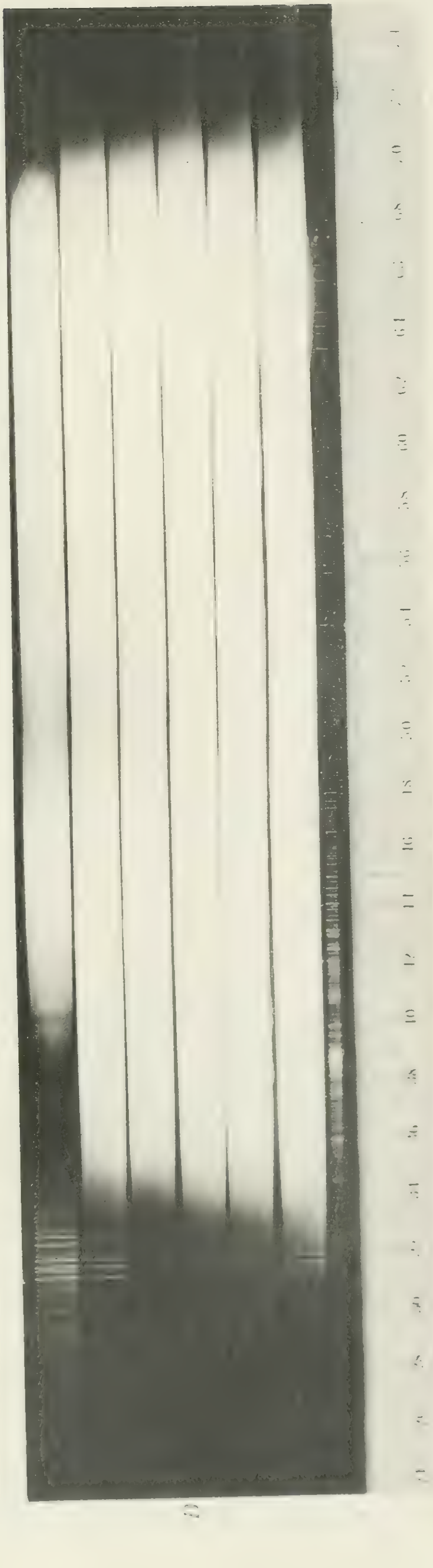

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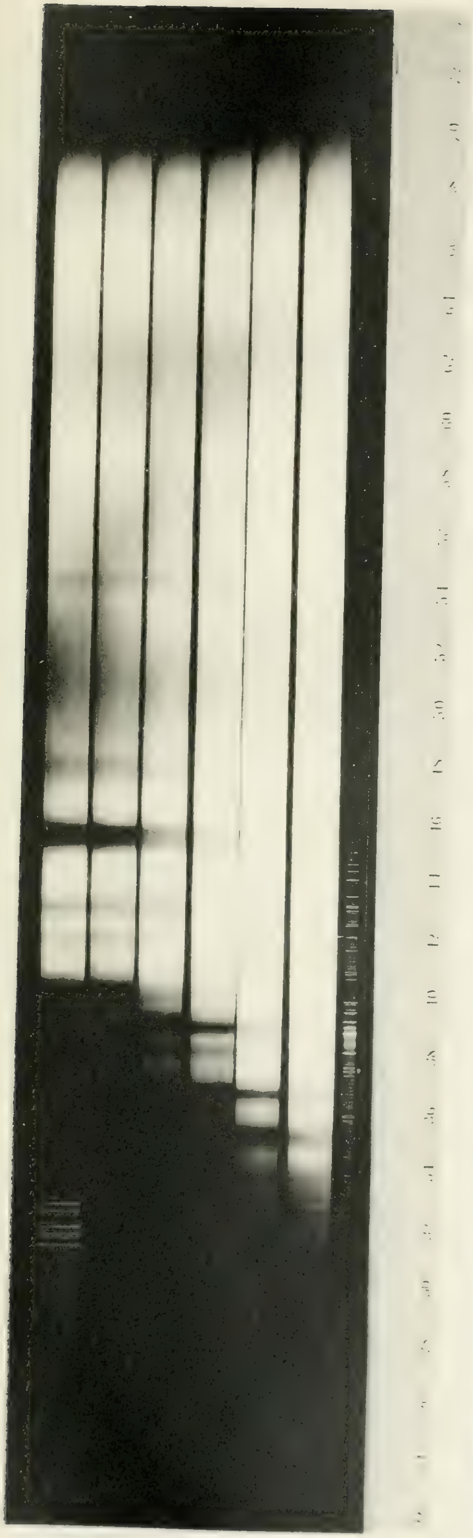
MERRELL ART CO., ELIZABETH, N. J.

PLATE 20



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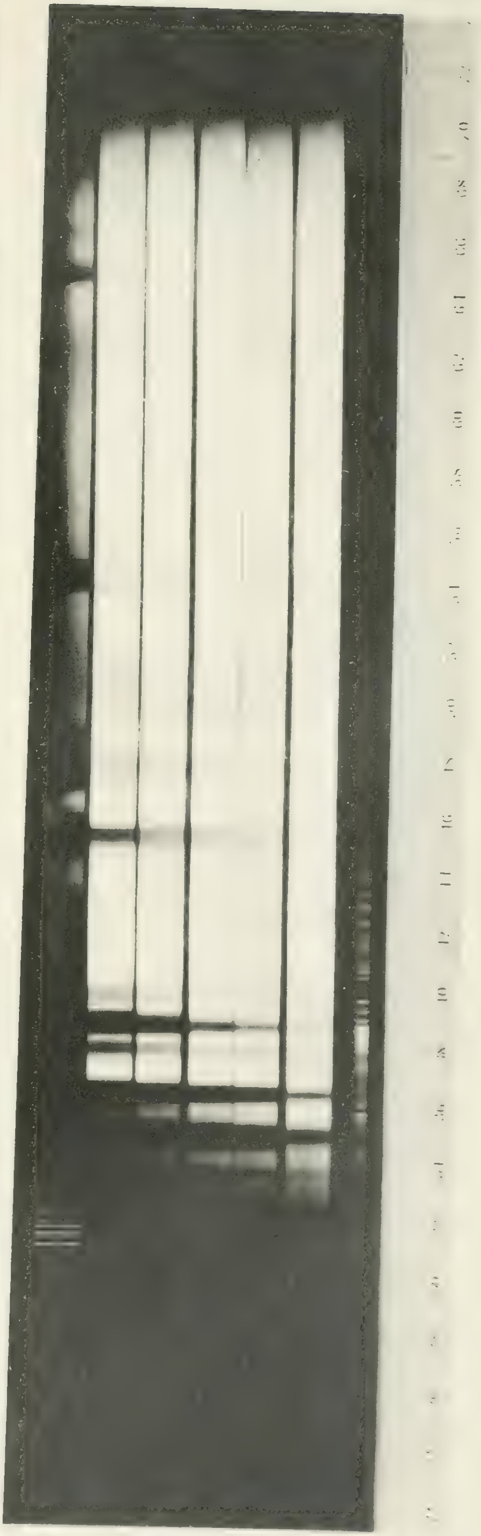

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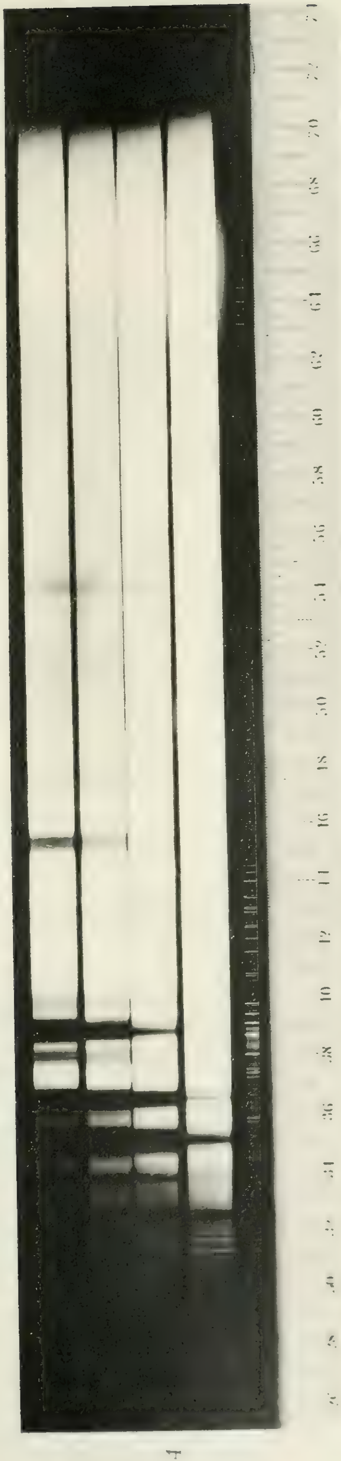
CAMPBELL ART CO., ELIZABETH, N. J.

PLATE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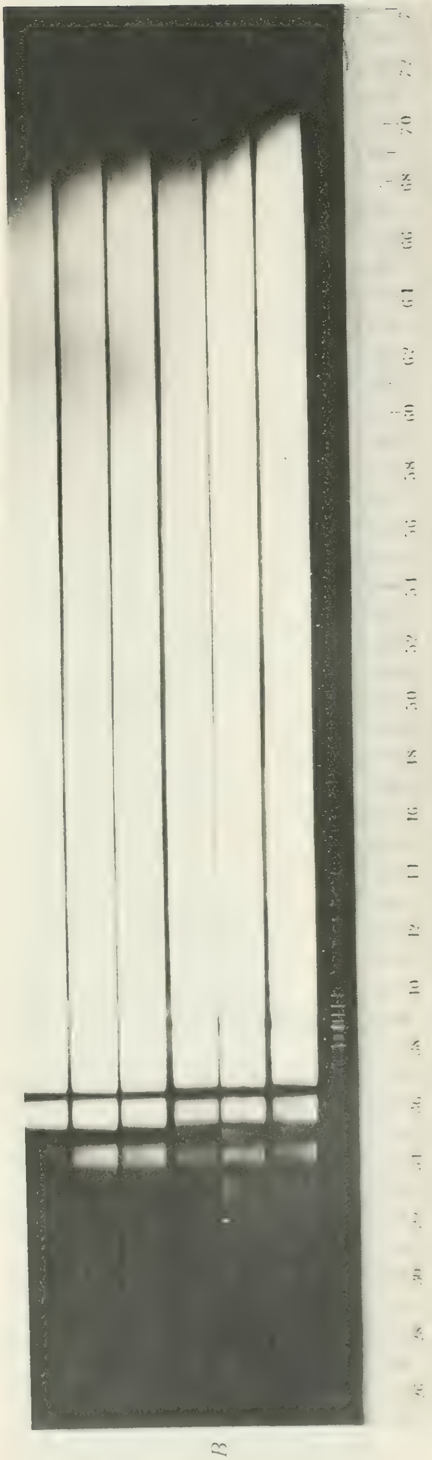
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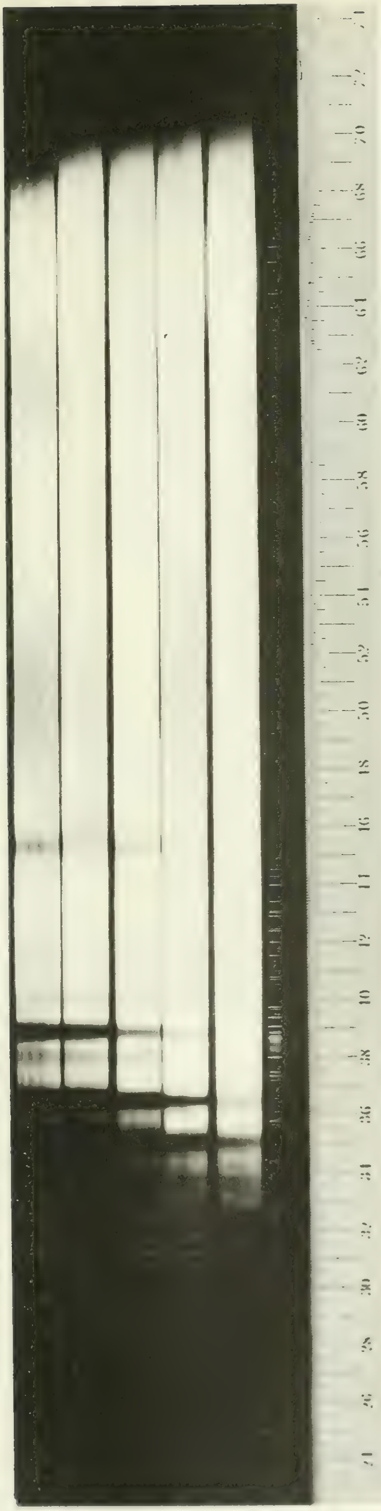
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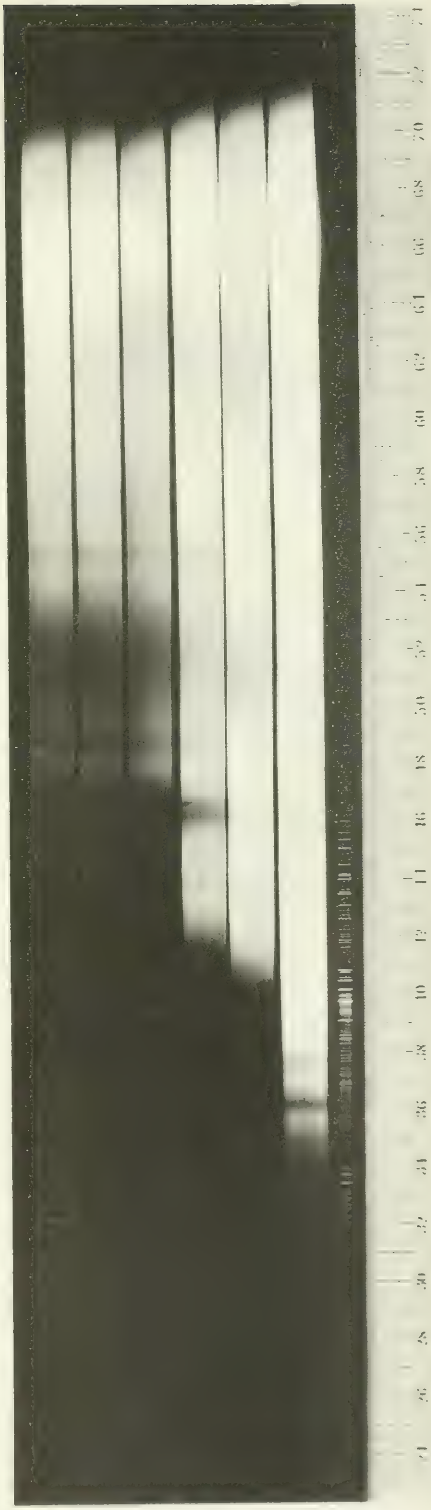
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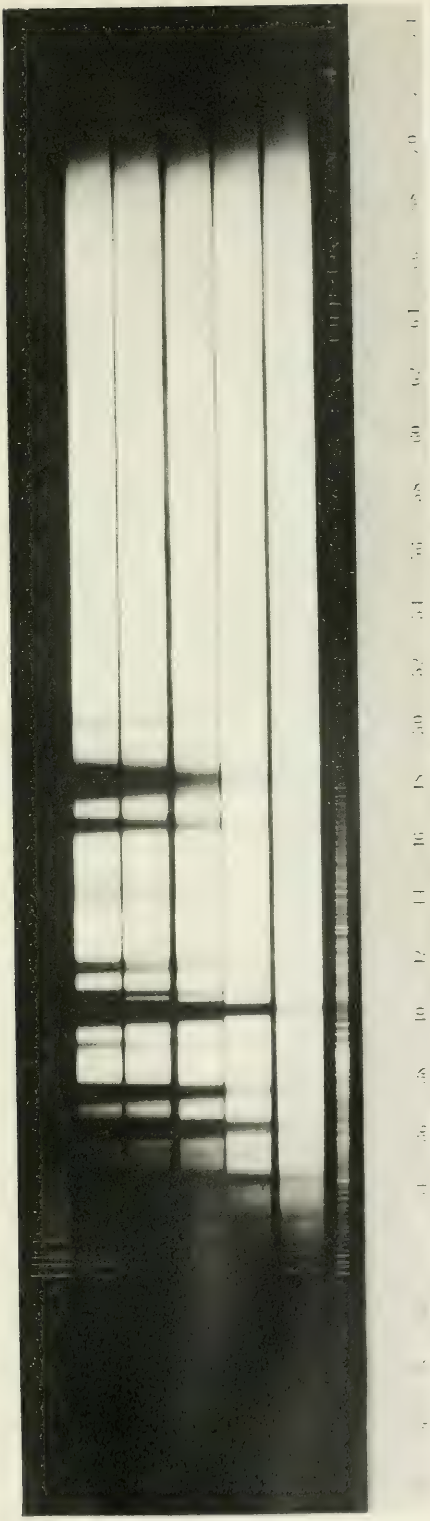

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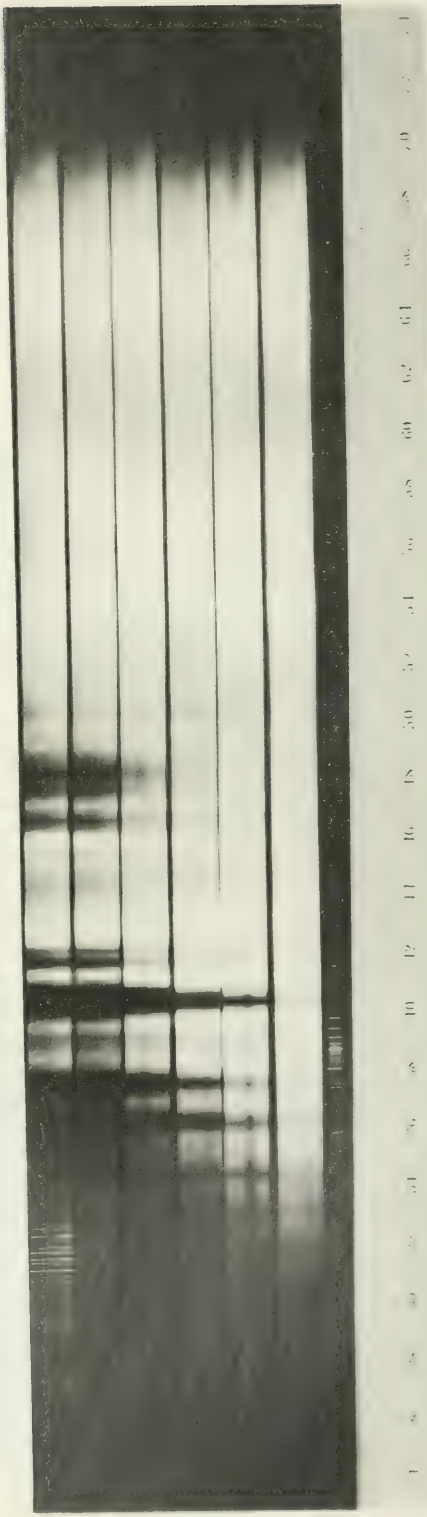

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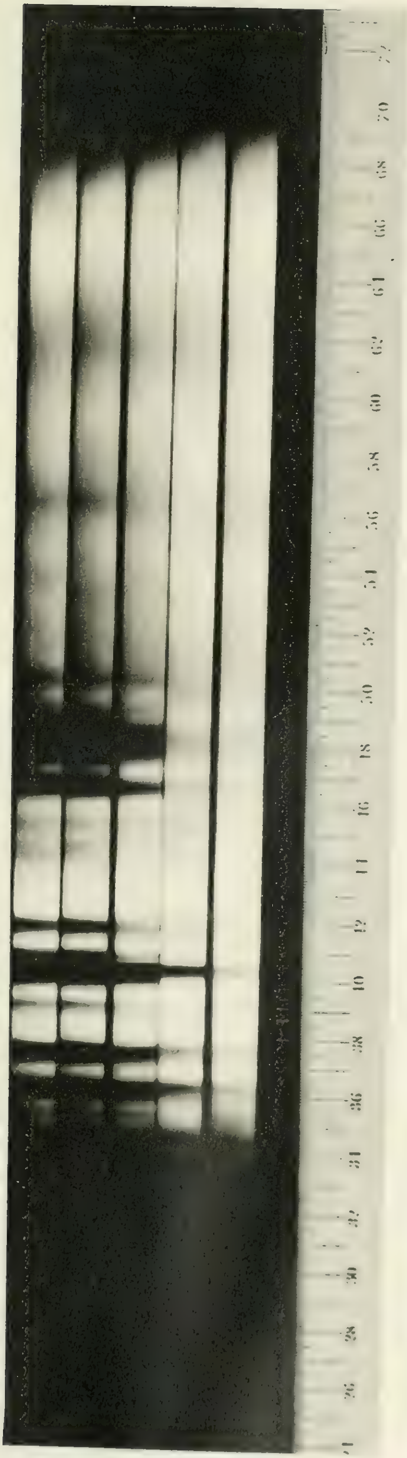
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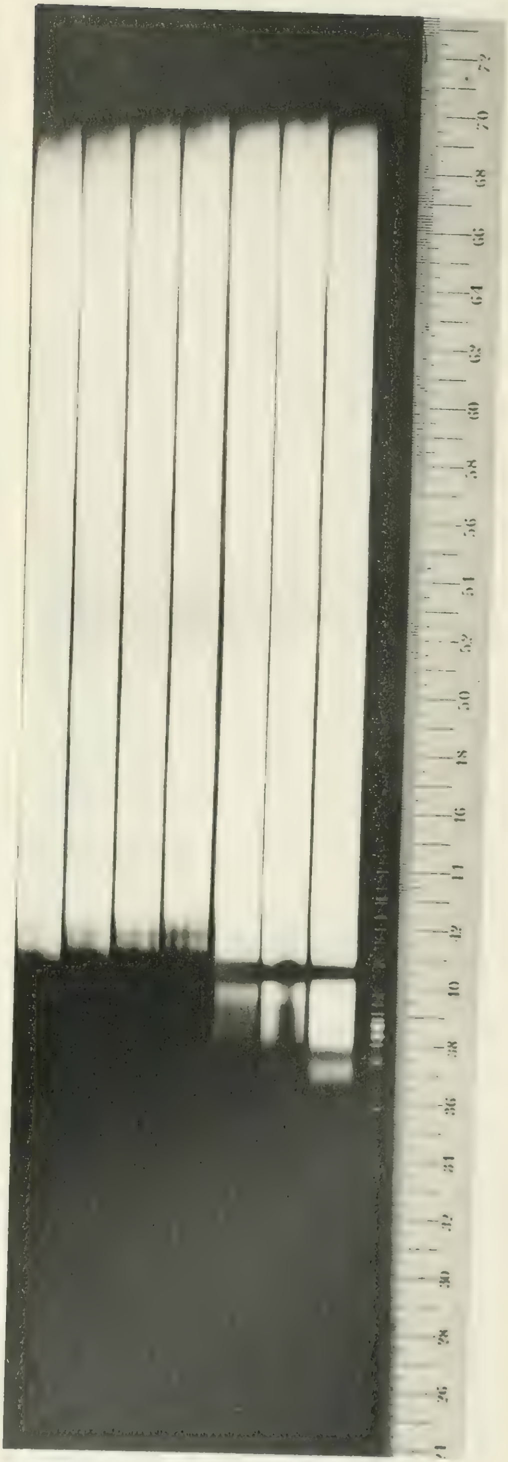
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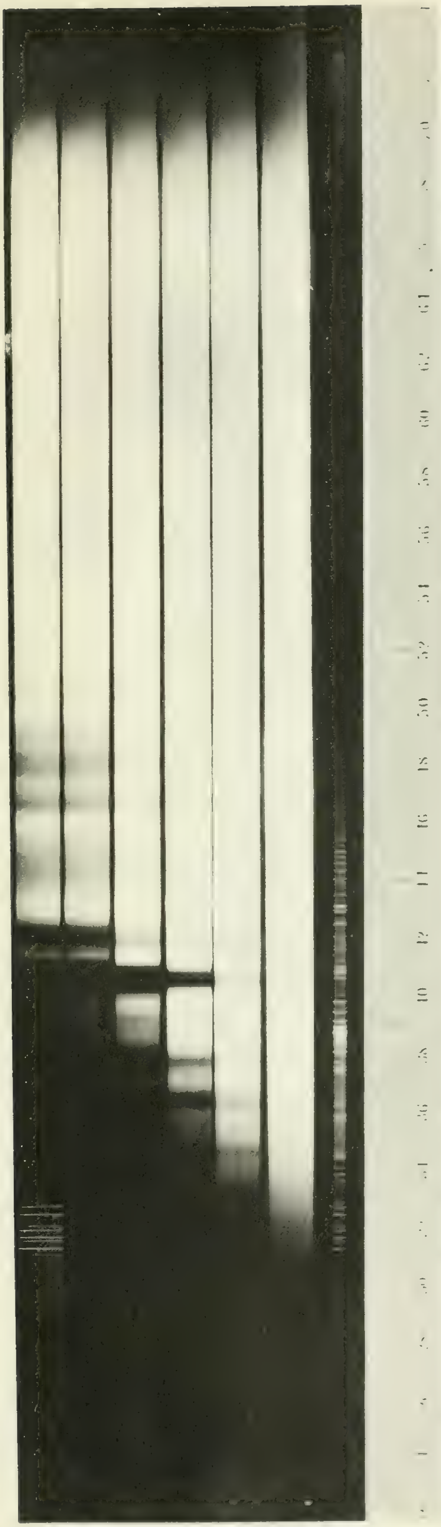

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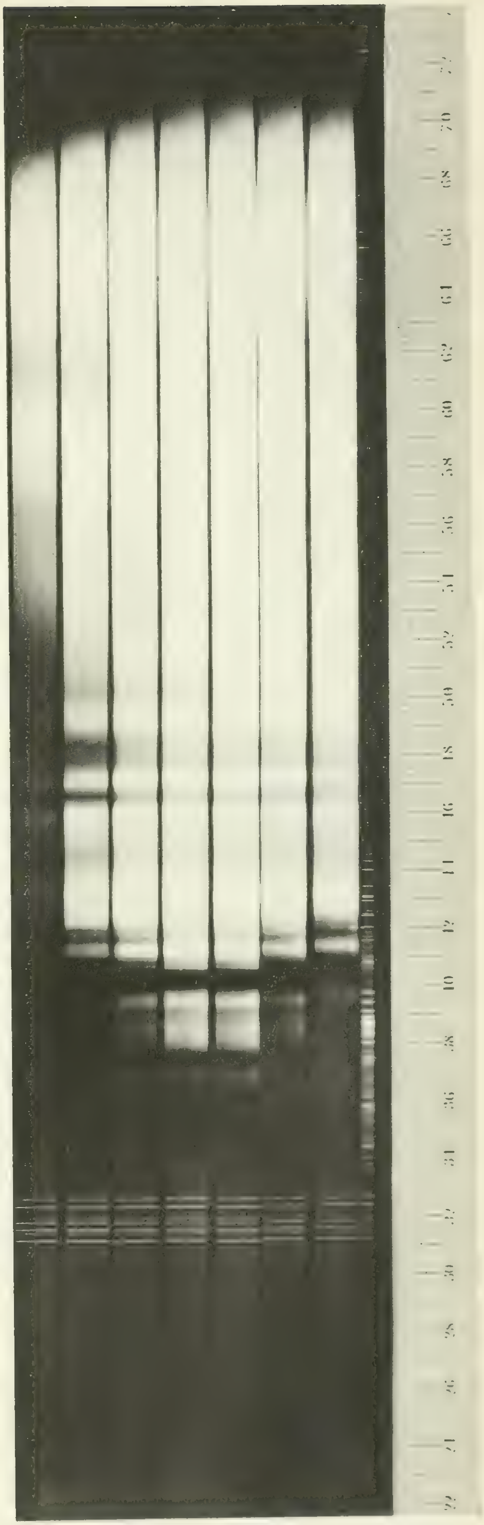

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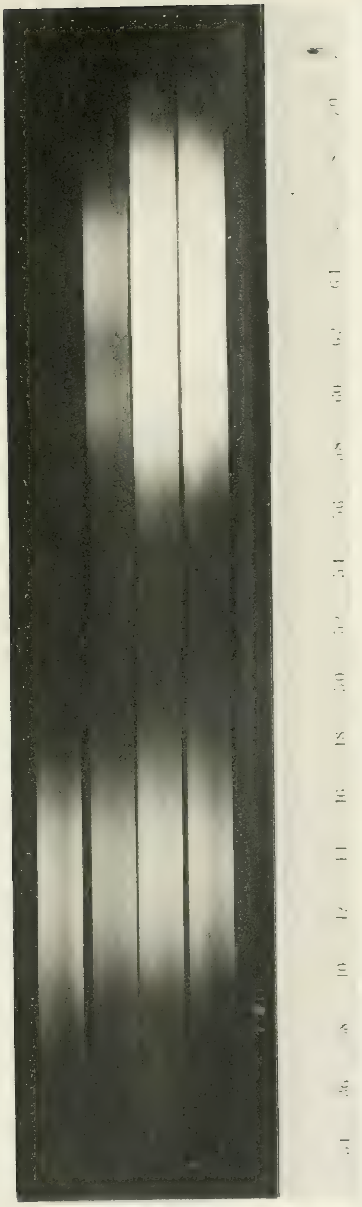

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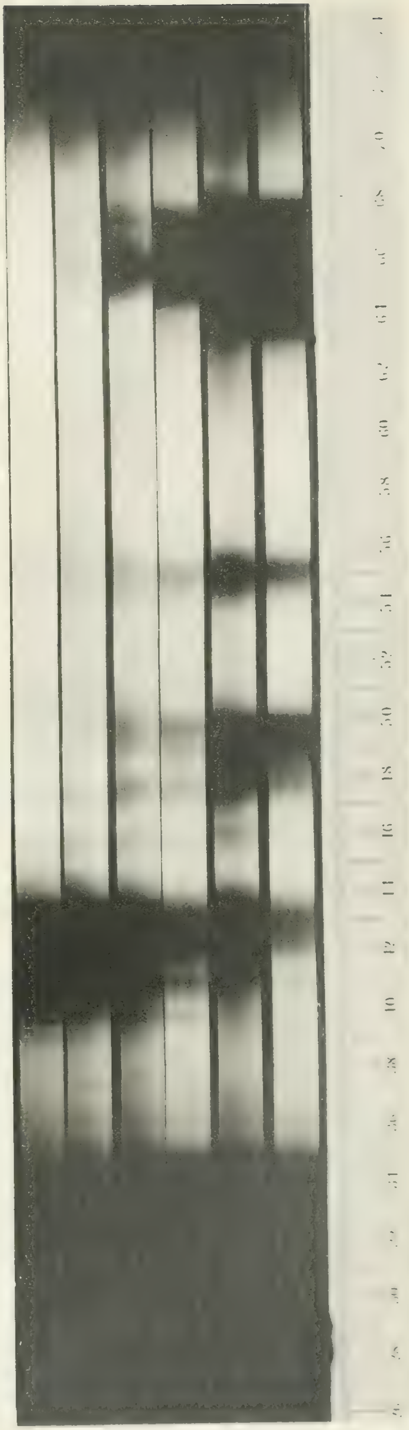

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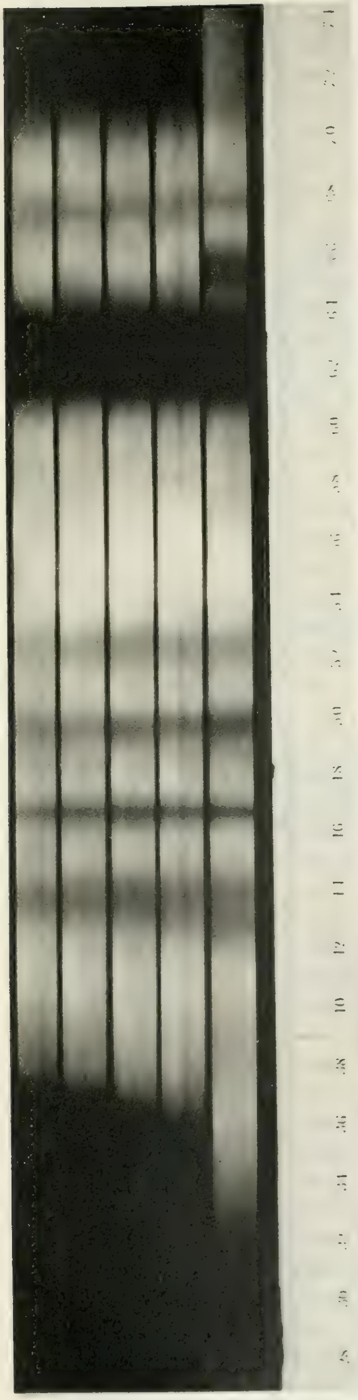

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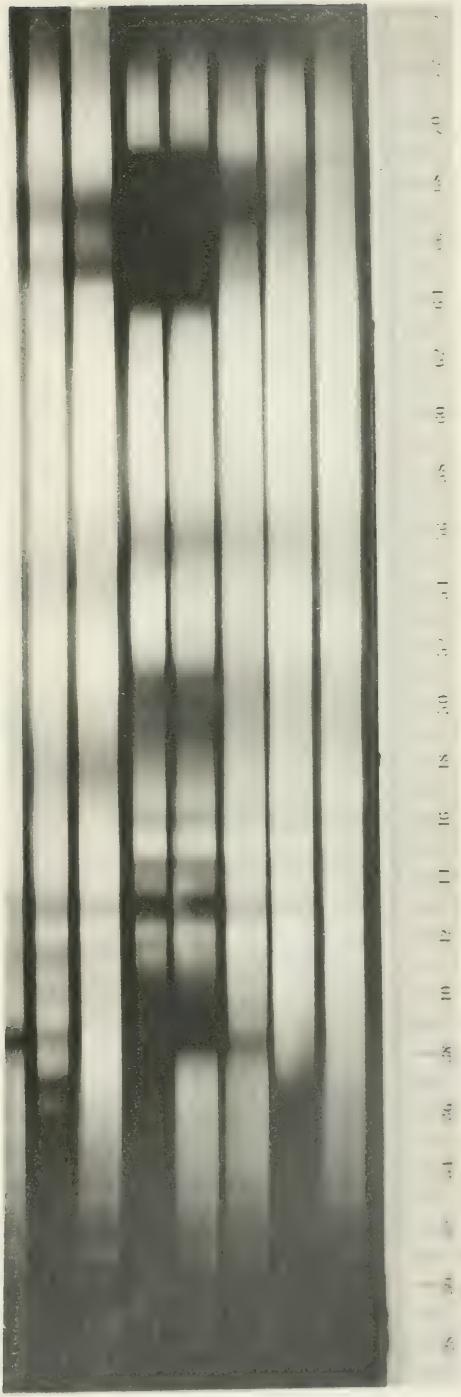

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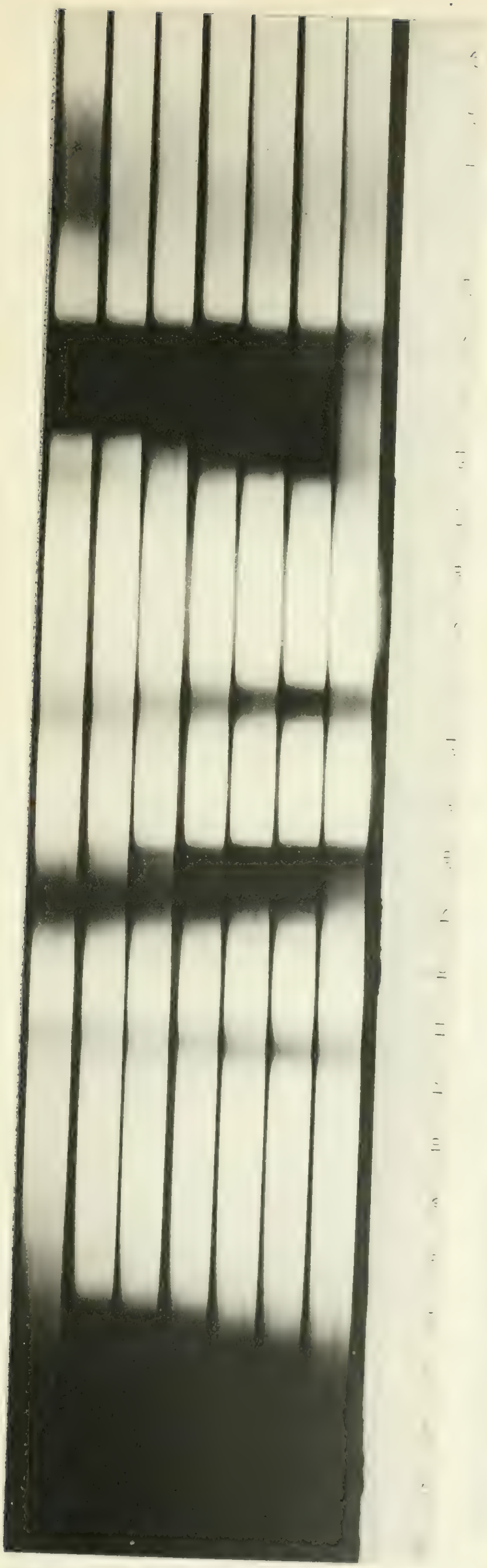

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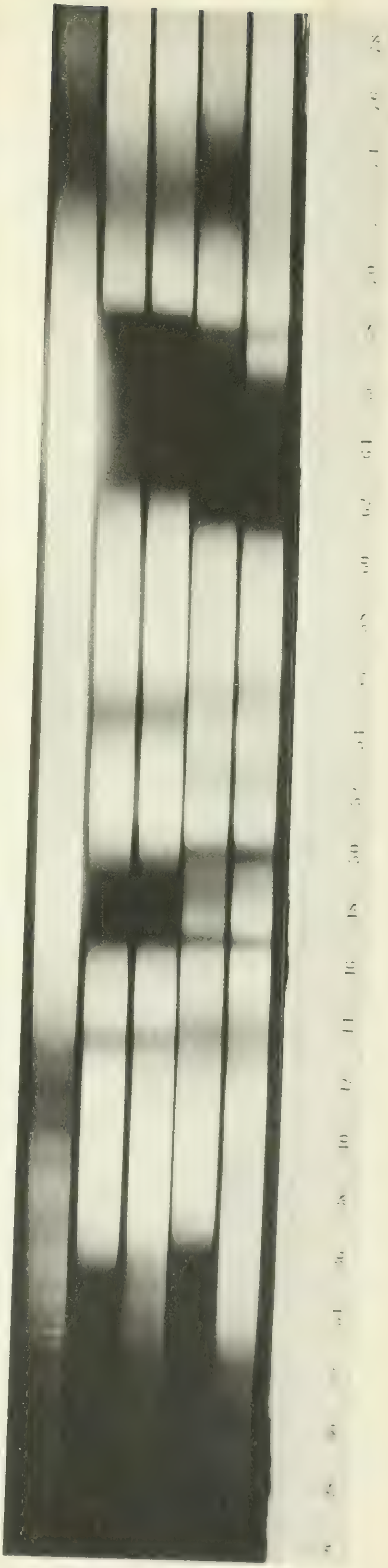

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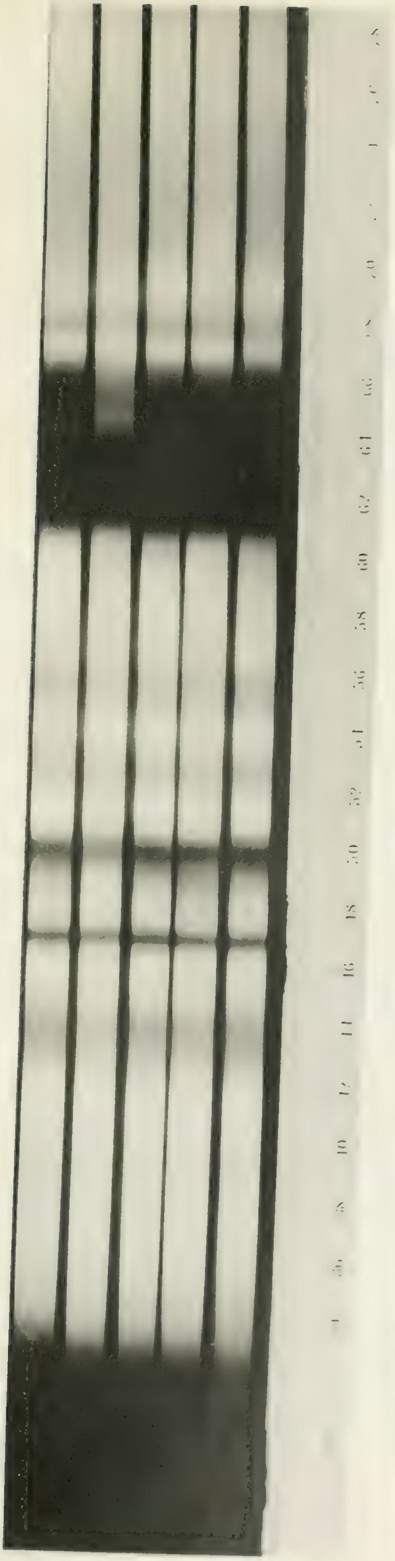

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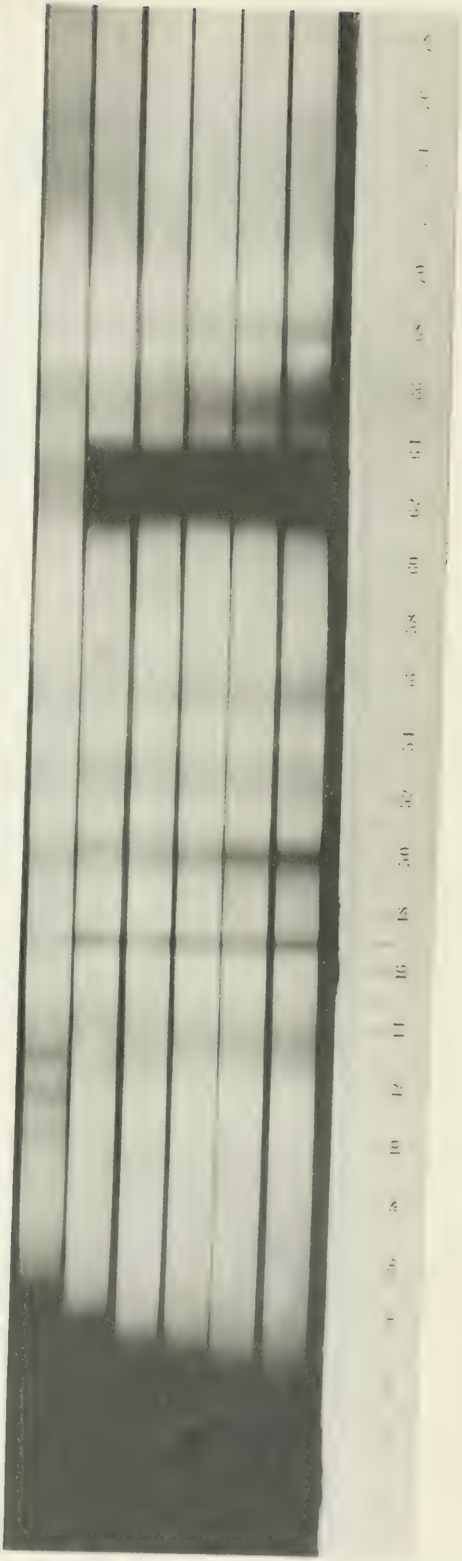

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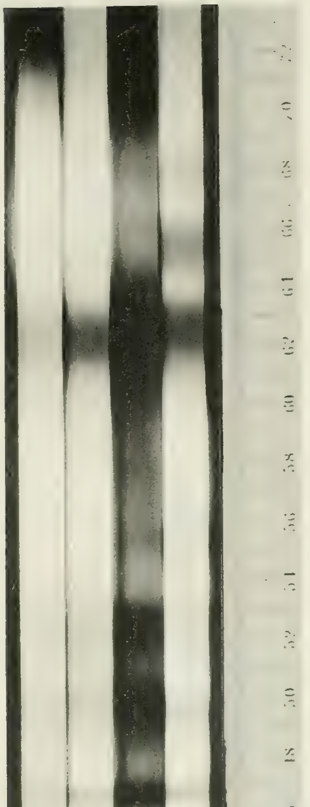
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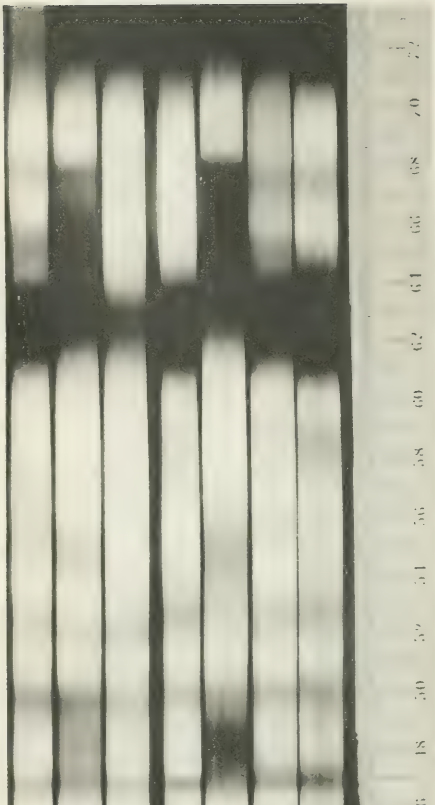
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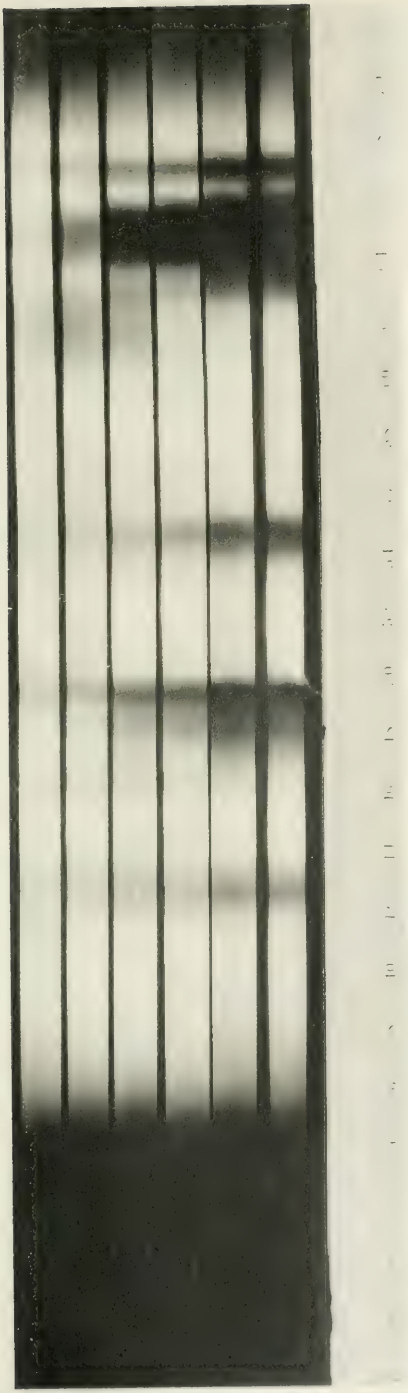

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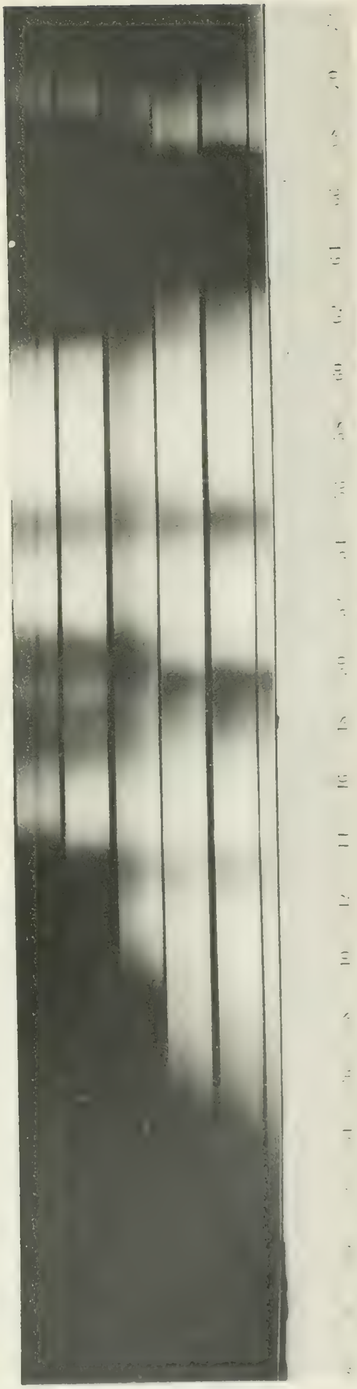

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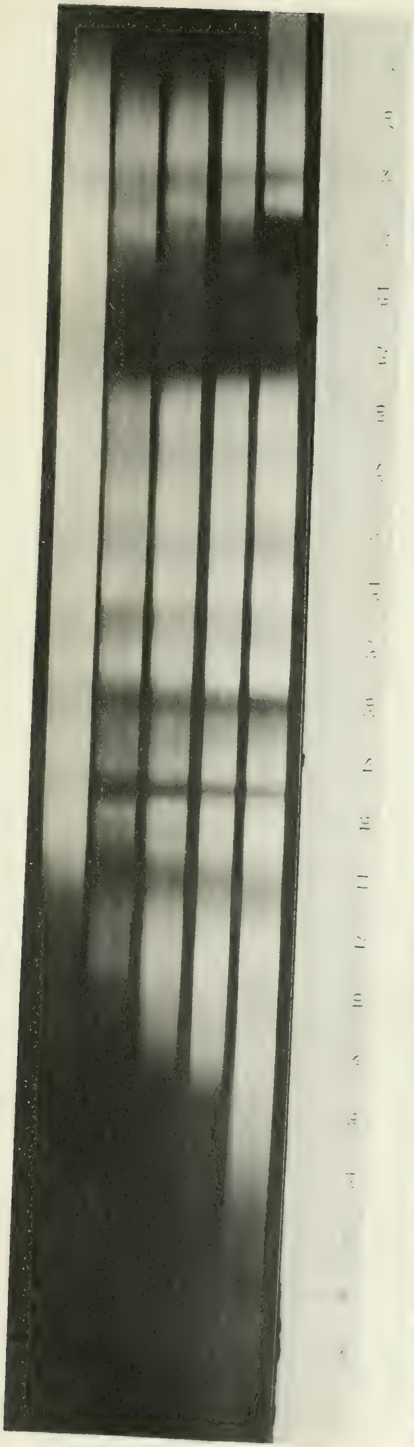
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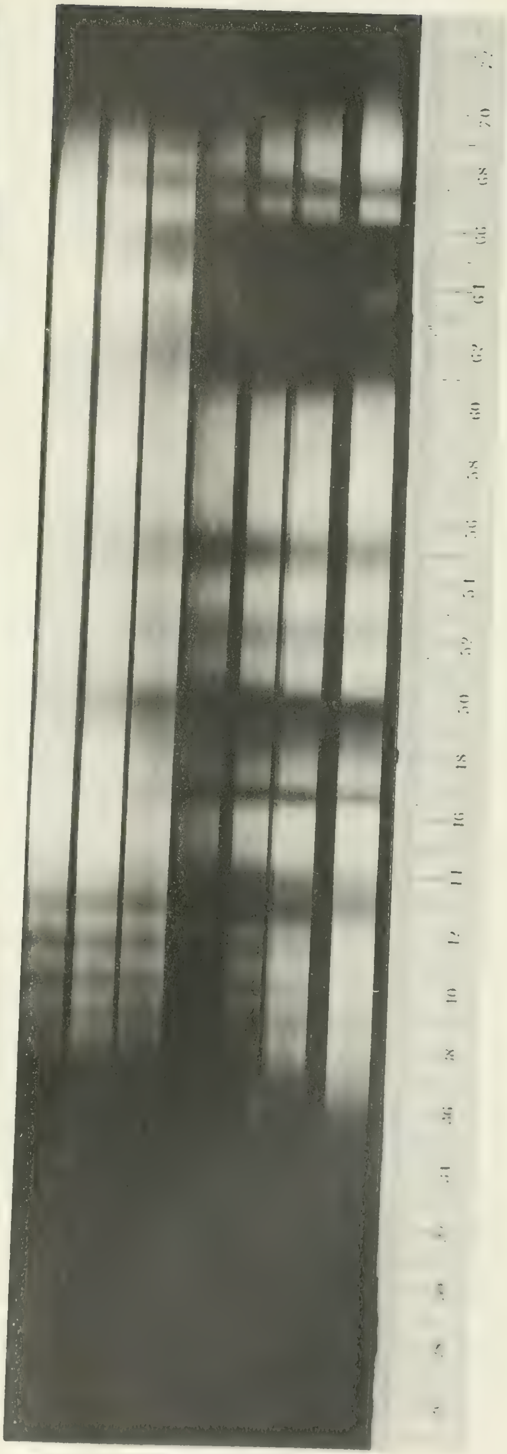
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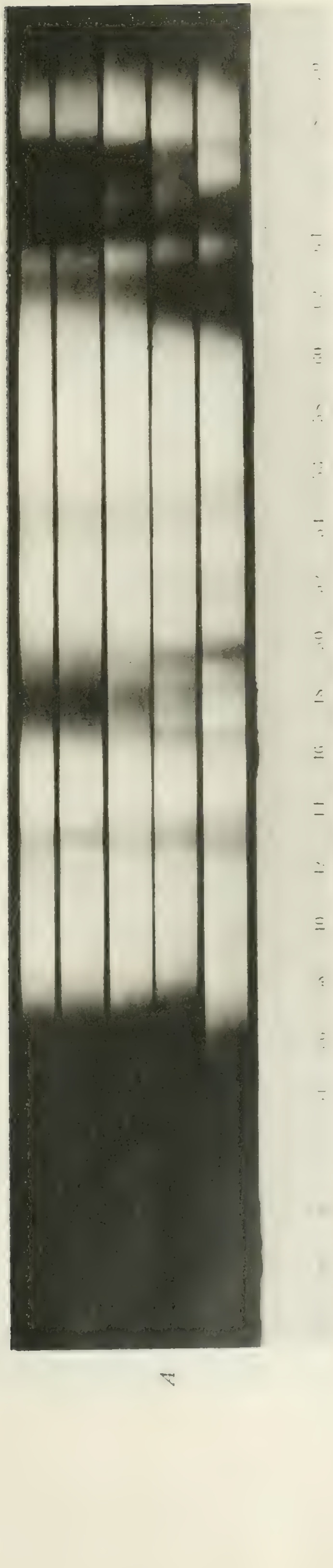

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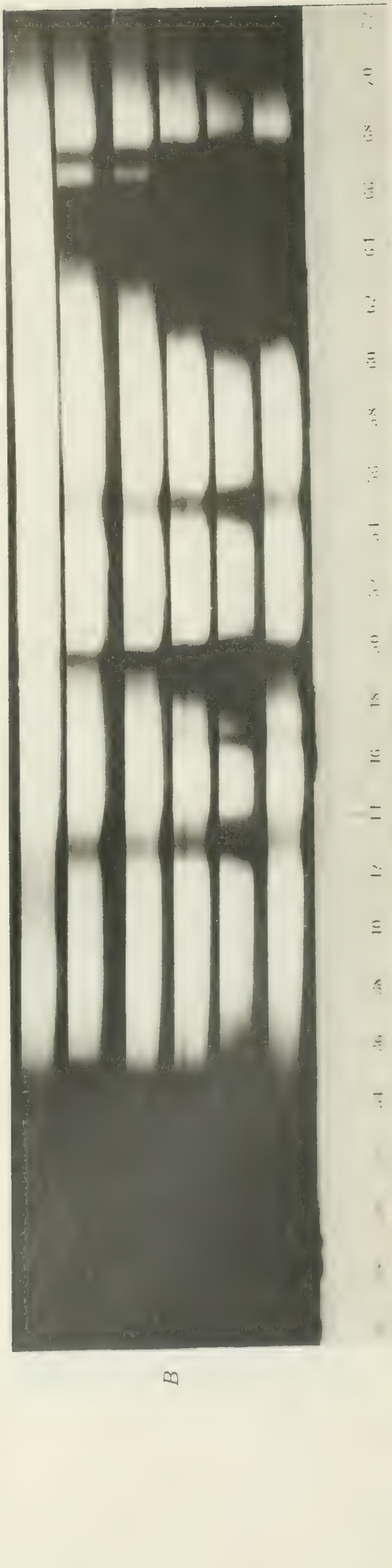

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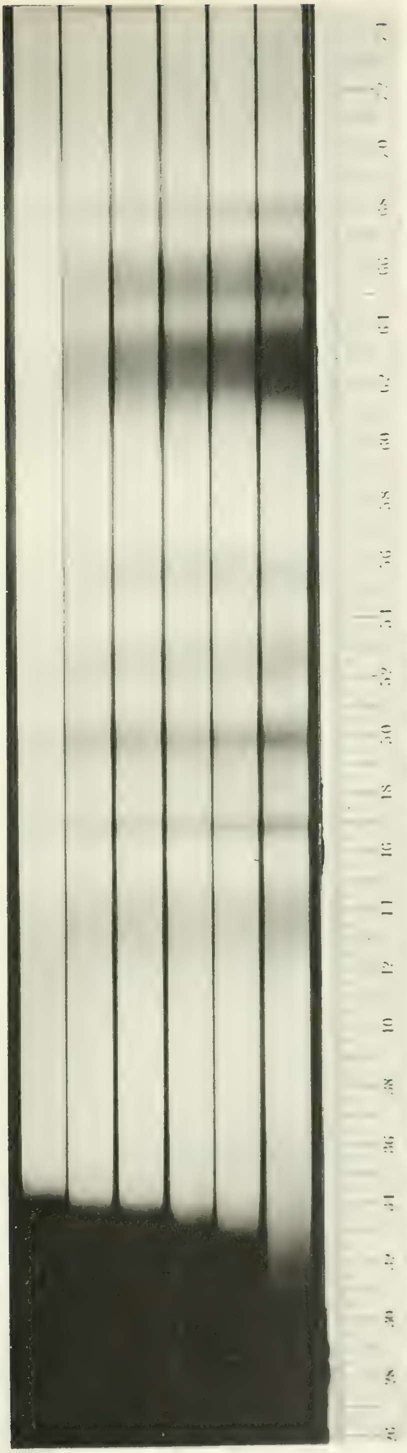

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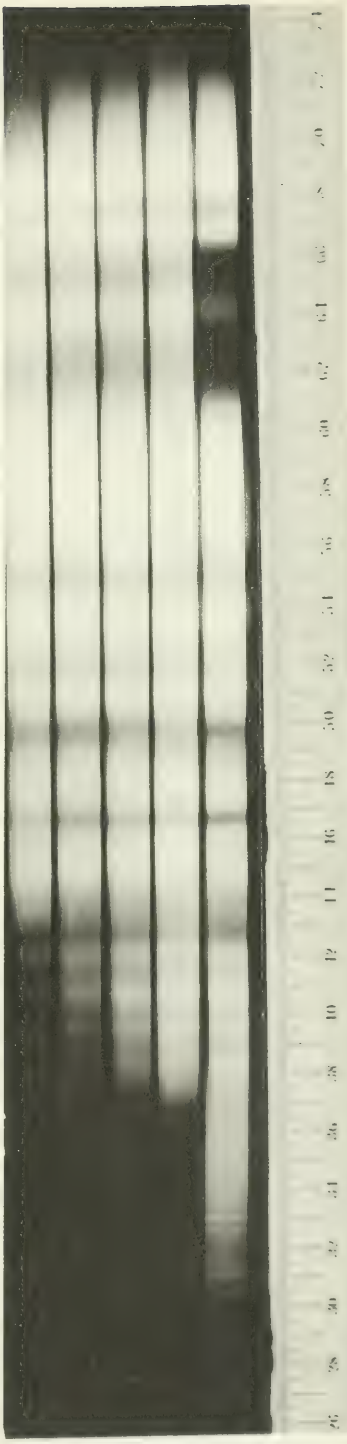

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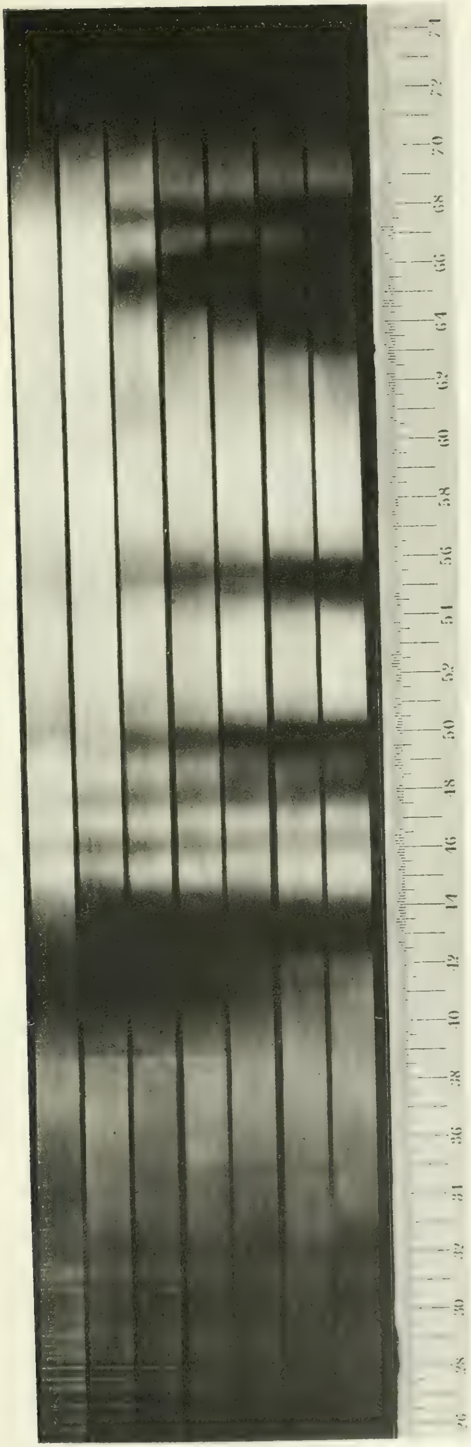
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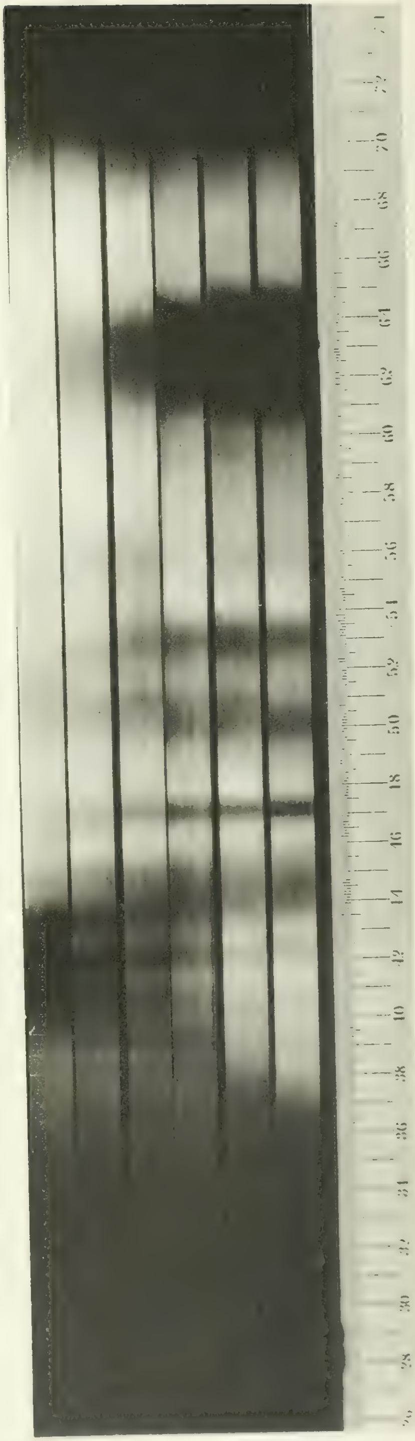
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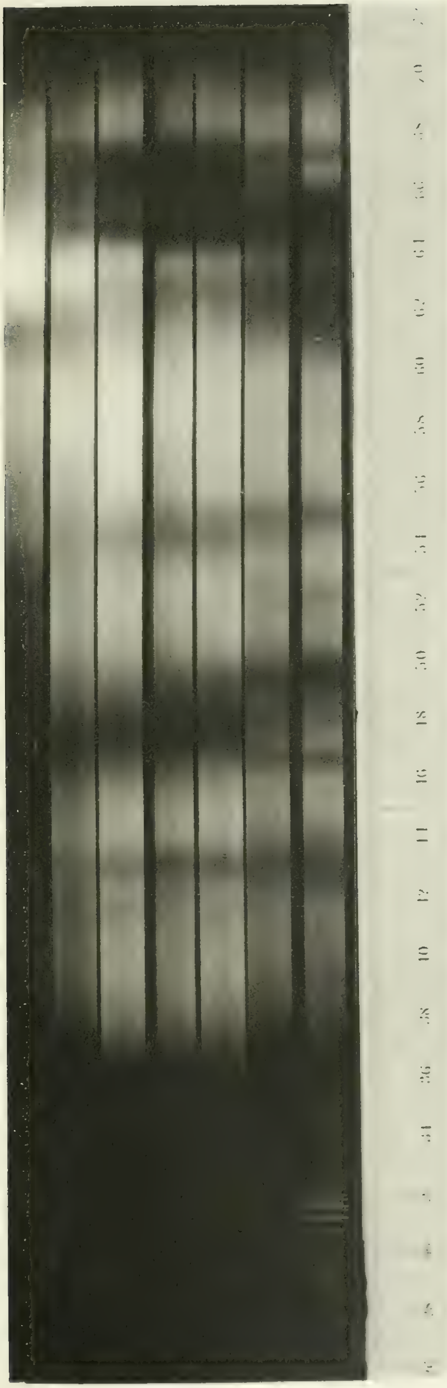

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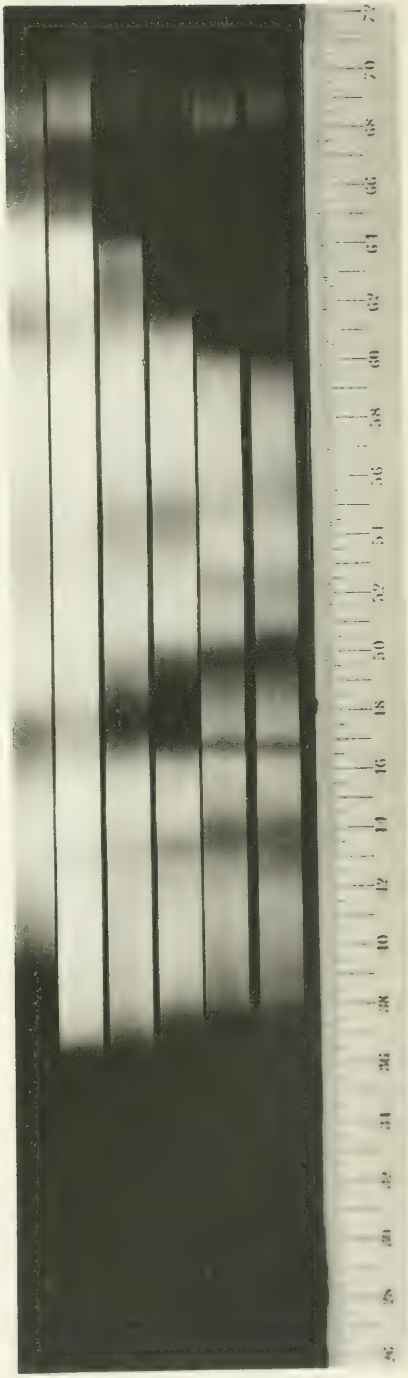

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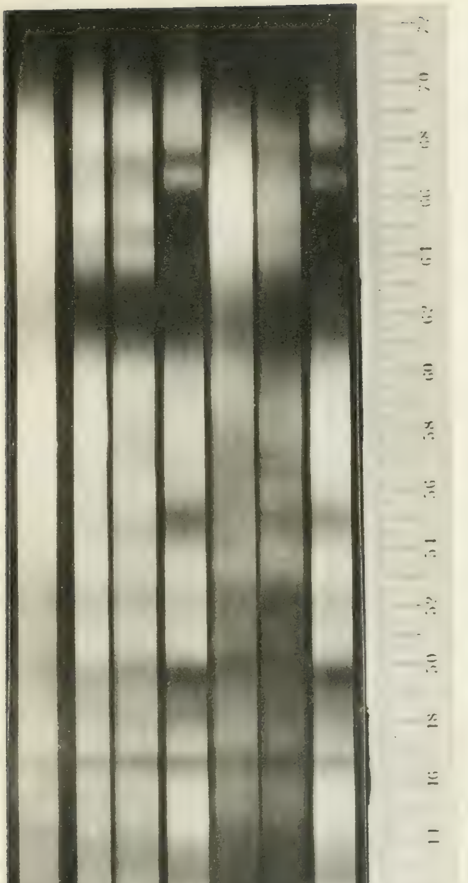
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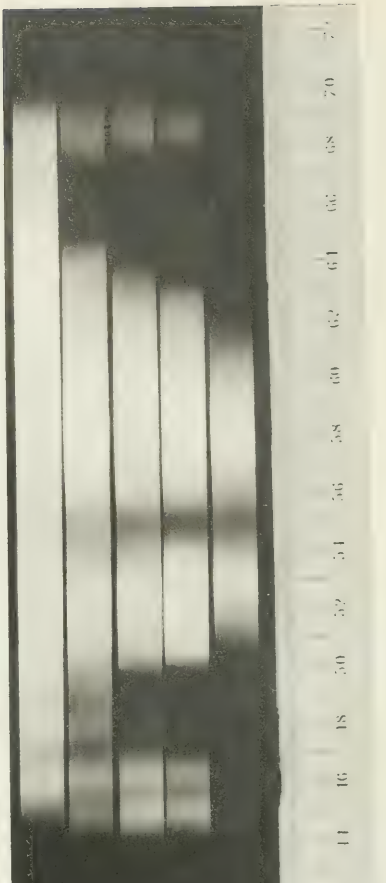
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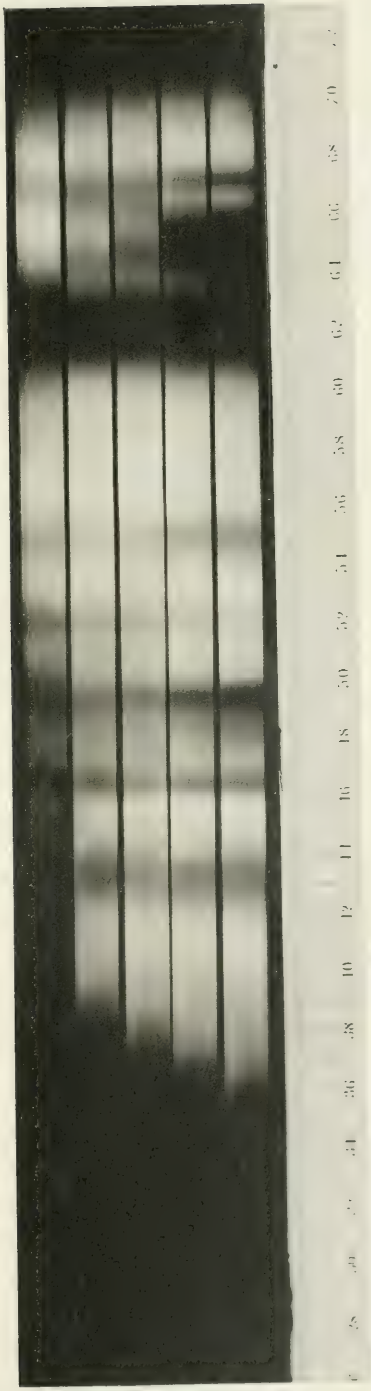
CAMPBELL ART CO. ELIZABETH, N. J.



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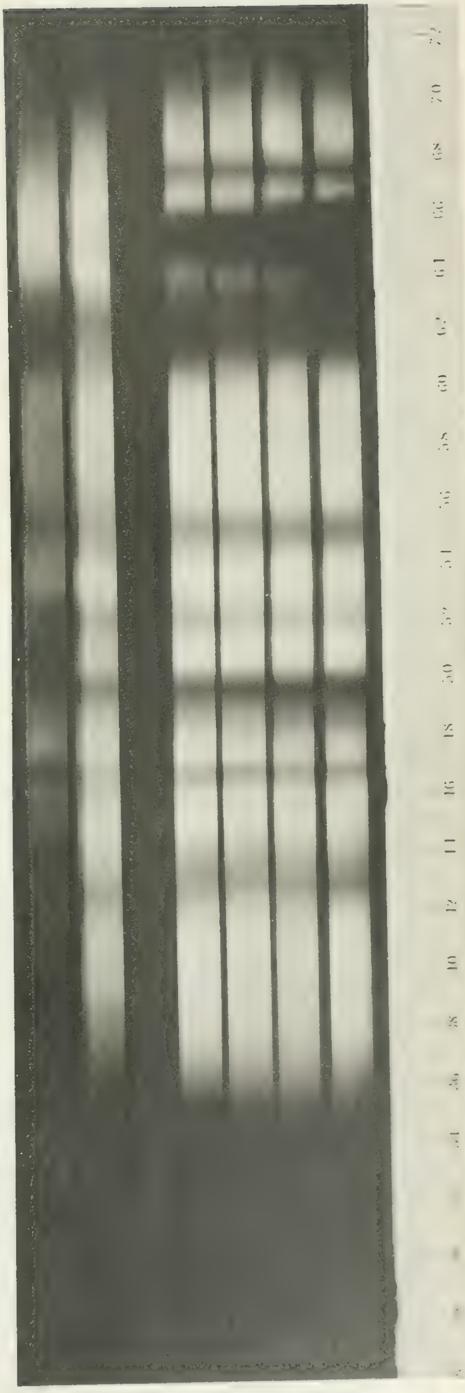

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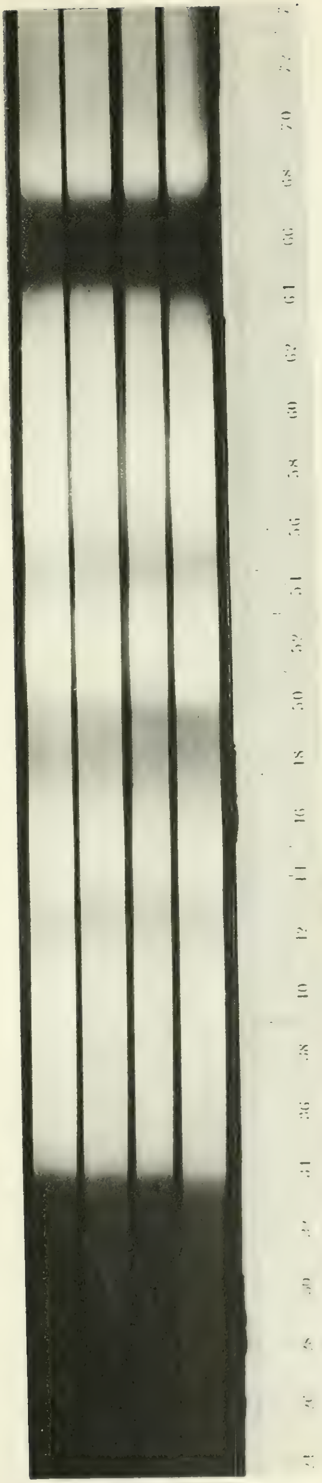
CAMPBELL ART CO., ELIZABETH, N. J.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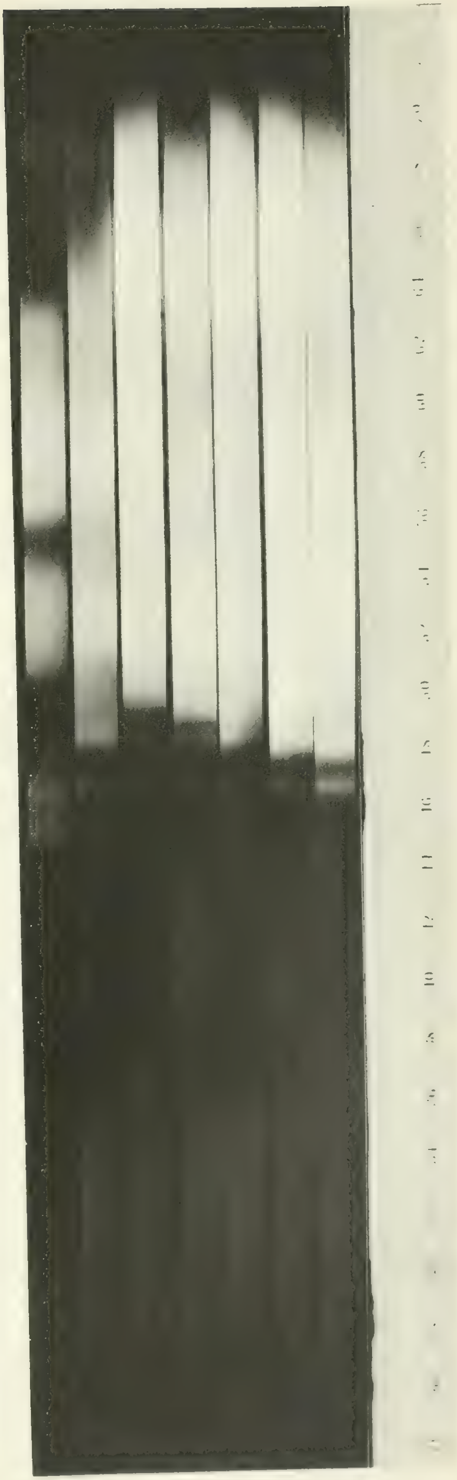
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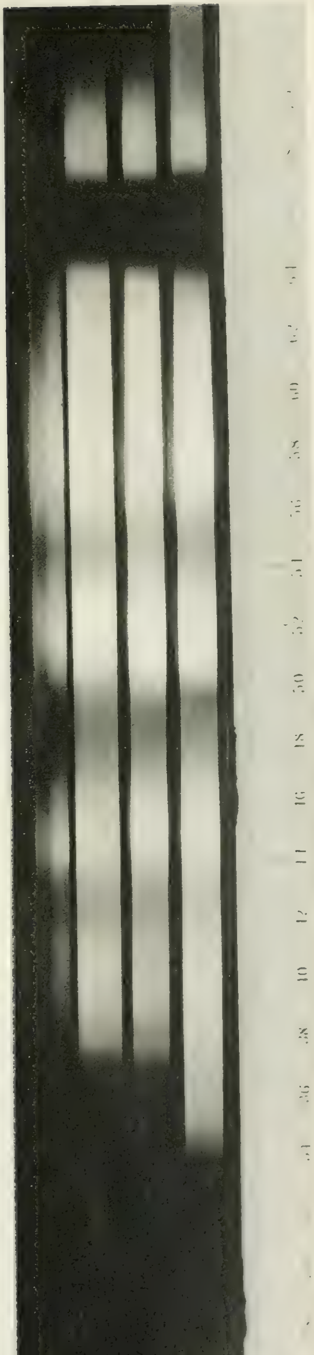
AMPBELL ART CO ELIZABETH N J



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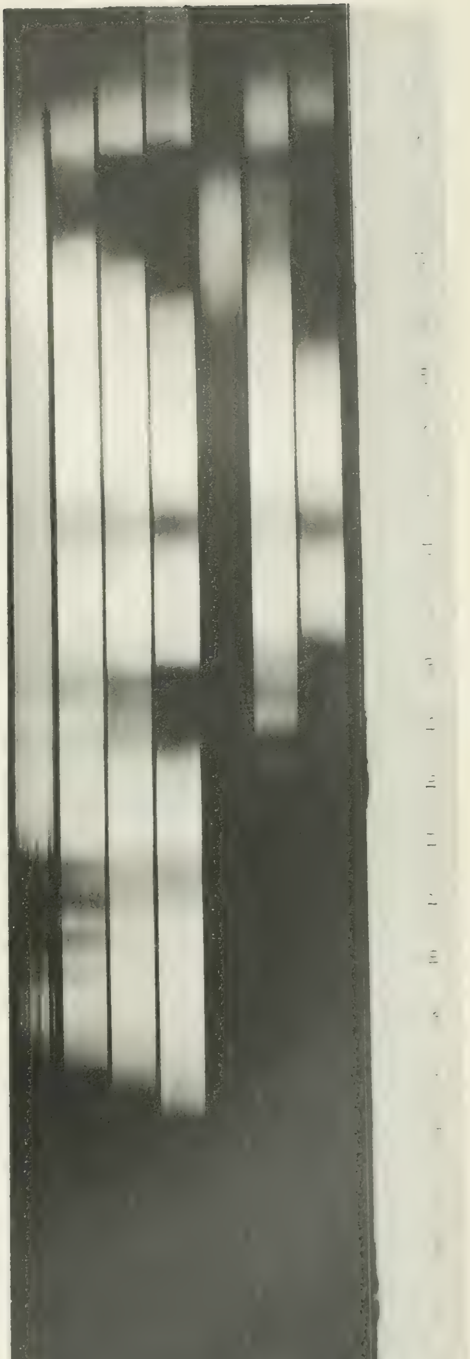

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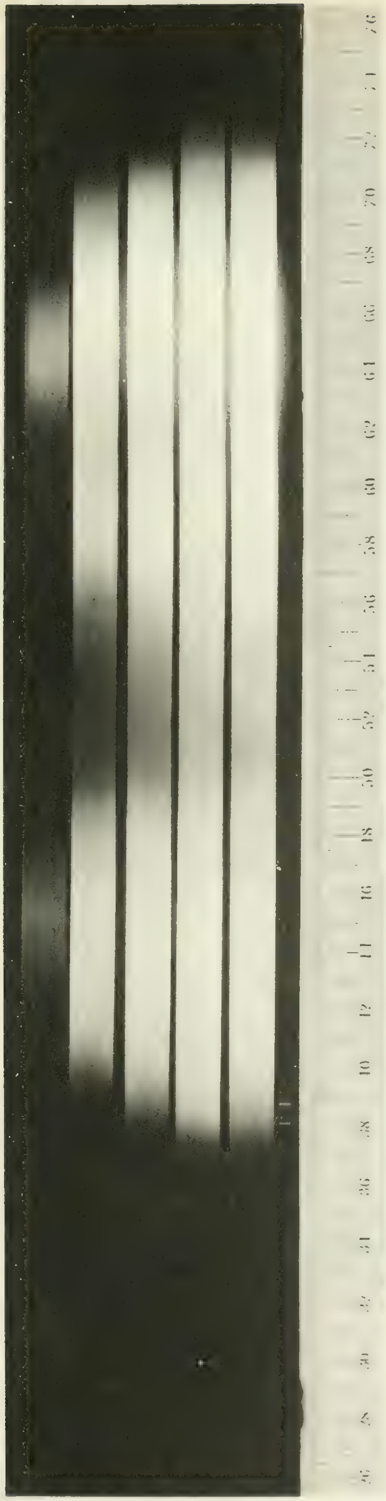
CAMPBELL ART CO ELIZABETH, N. J.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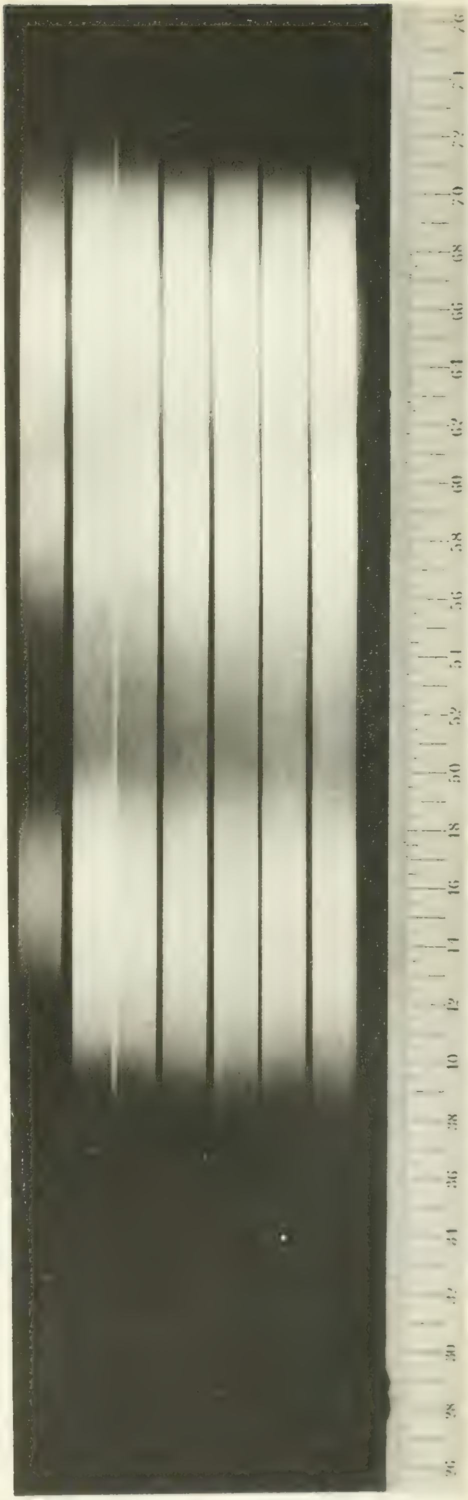
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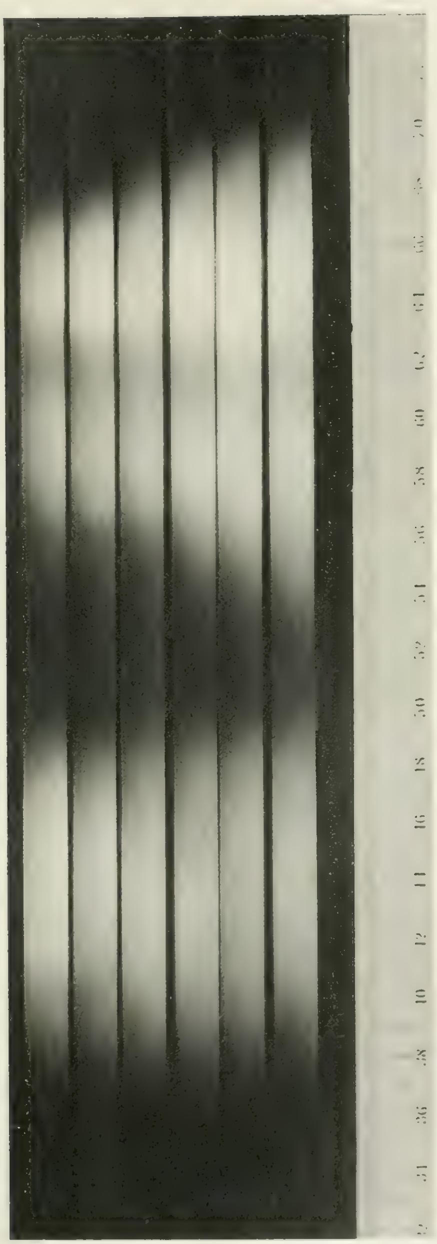
CAMPBELL ART CO., ELIZABETH, N. J.



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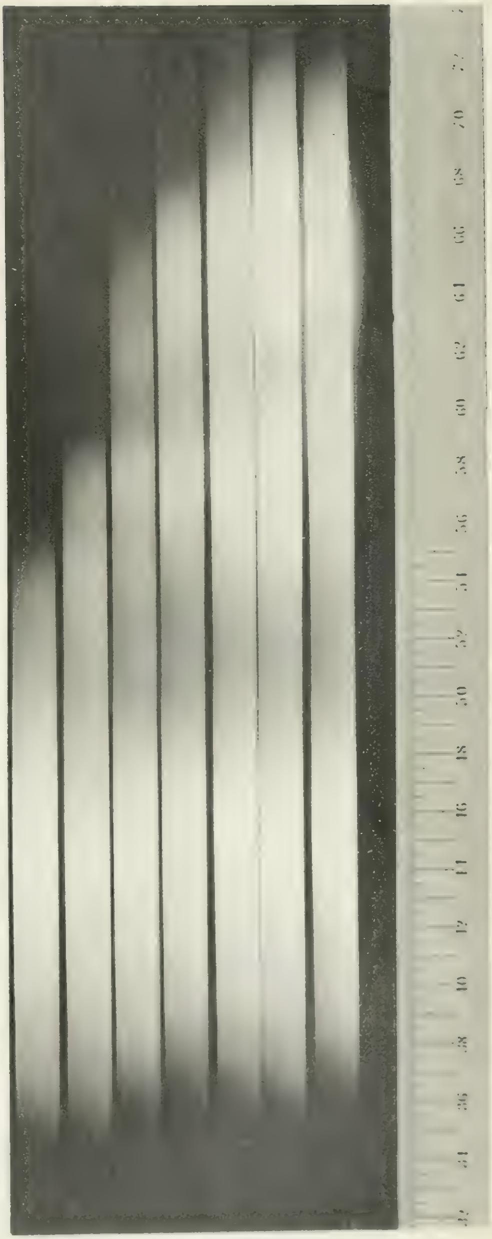

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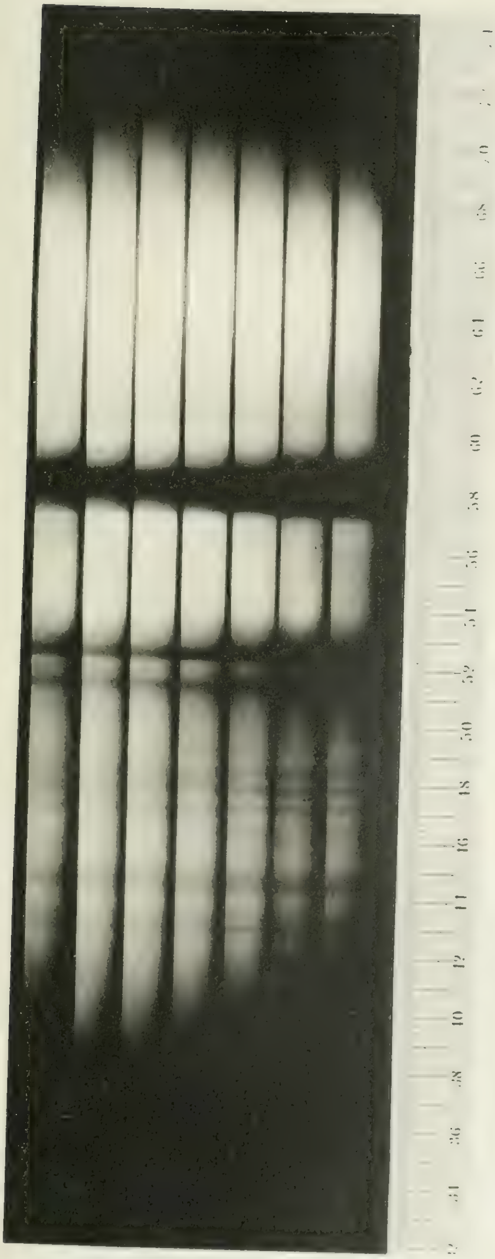
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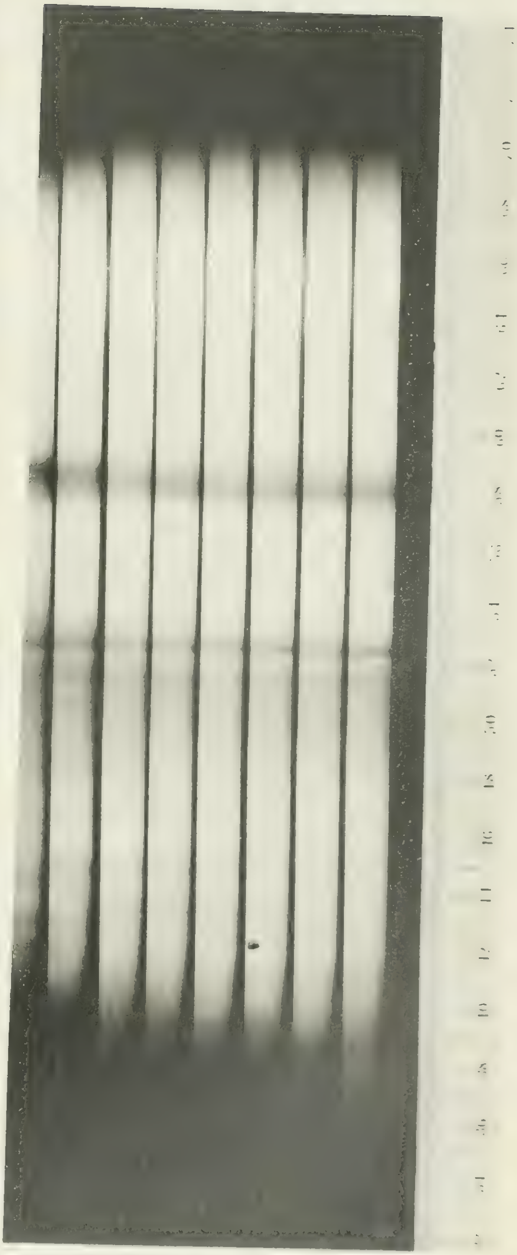
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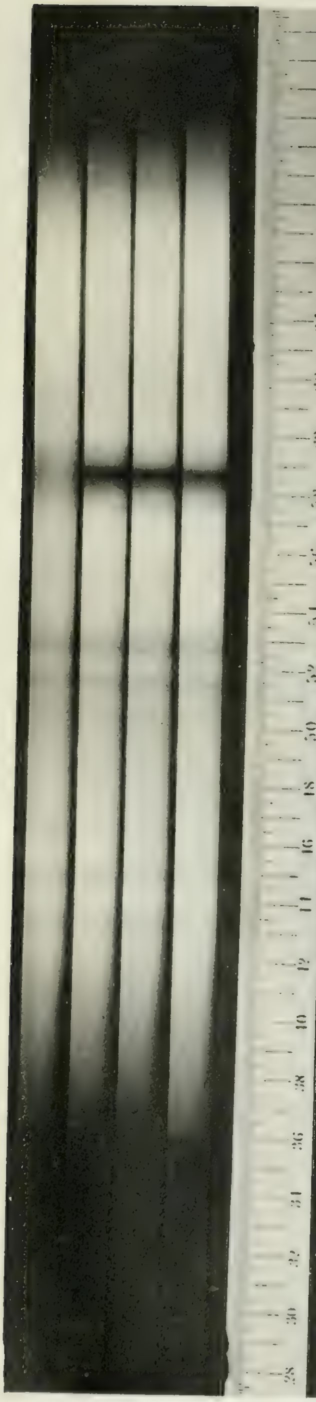
CAMPBELL ART CO., ELIZABETH, N. J.

PLATE 53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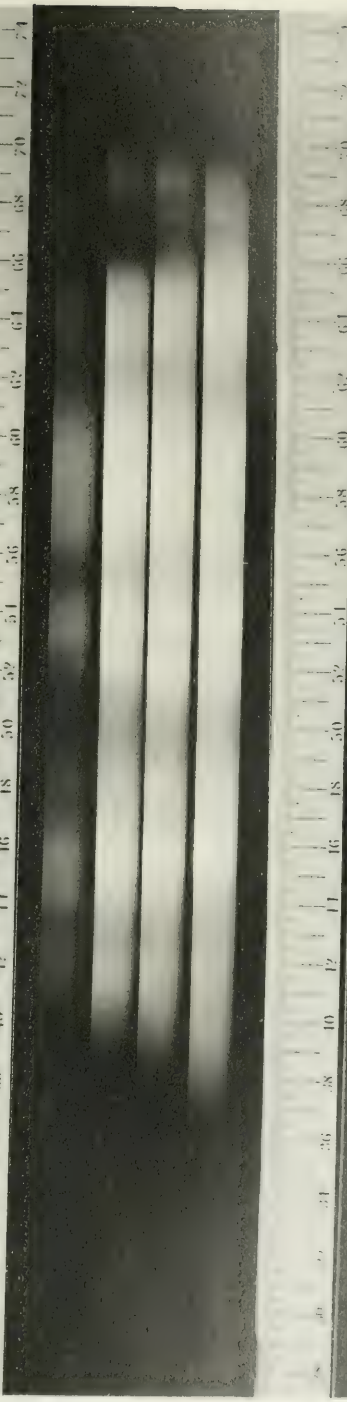
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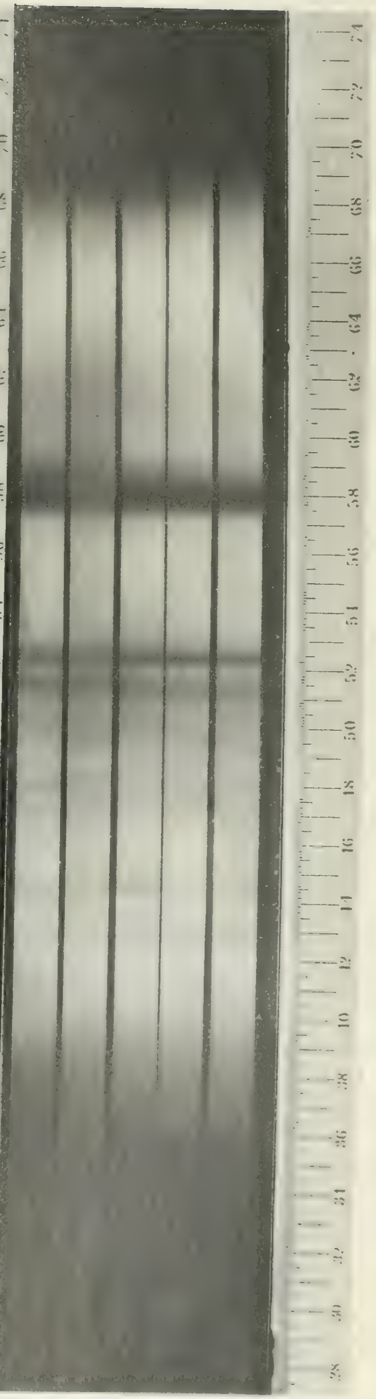
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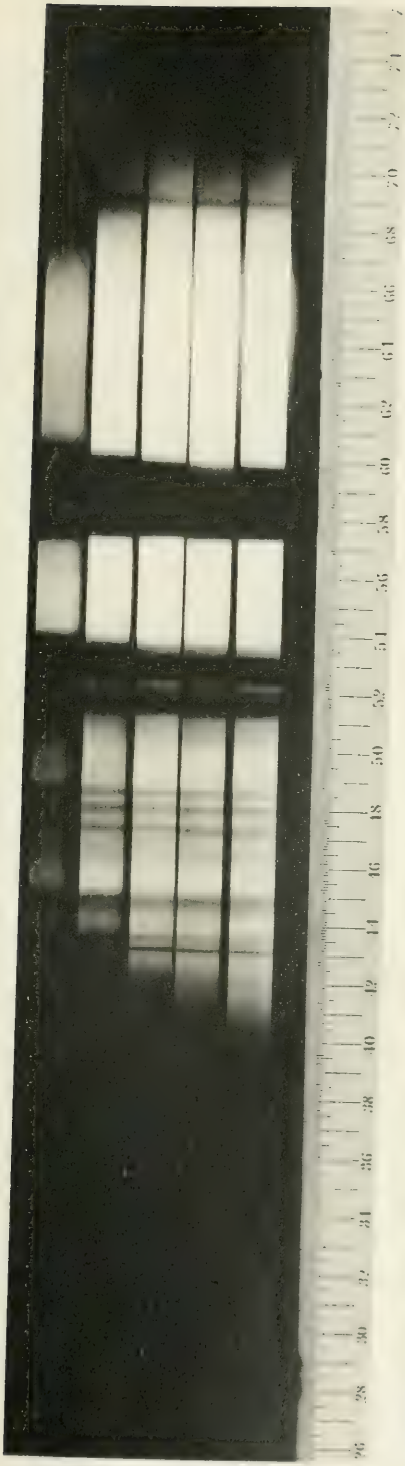
CAMPBELL ART CO., ELIZABETH, N. J.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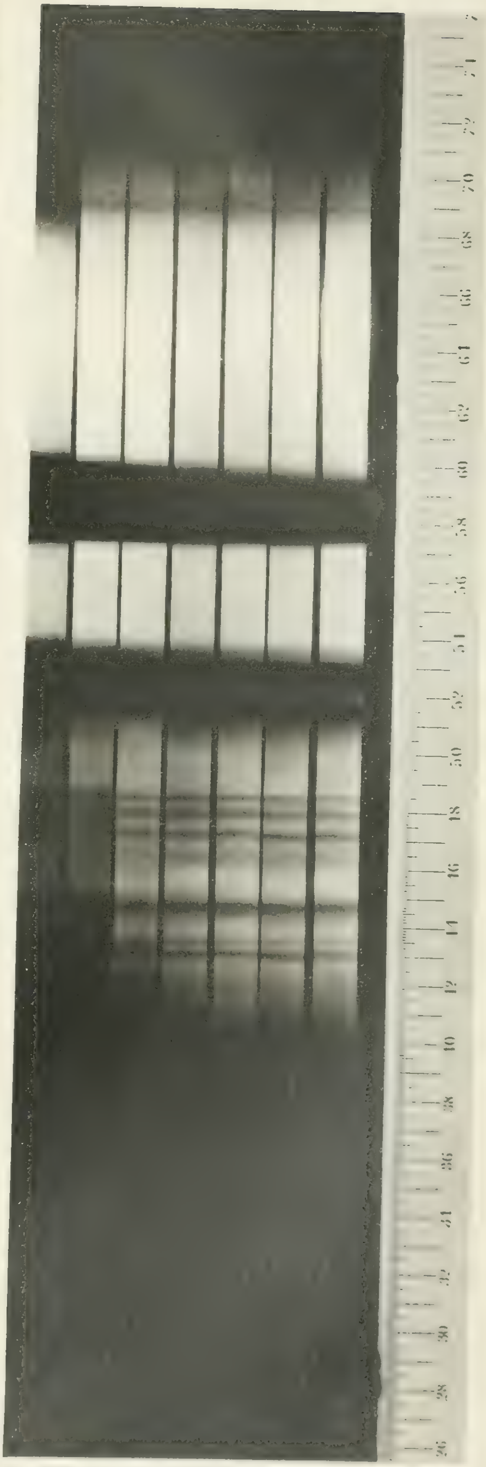
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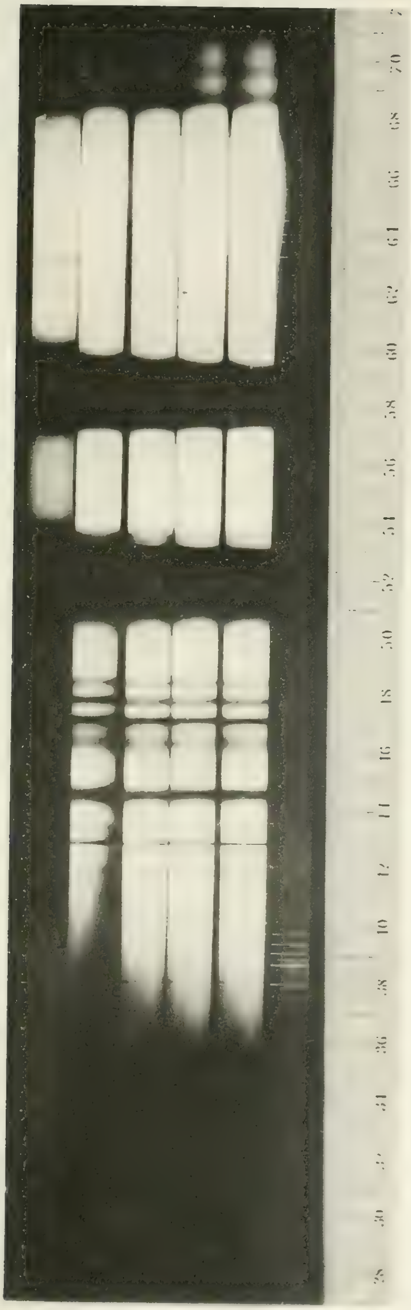
CAMPBELL ART CO., ELIZABETH, N. J.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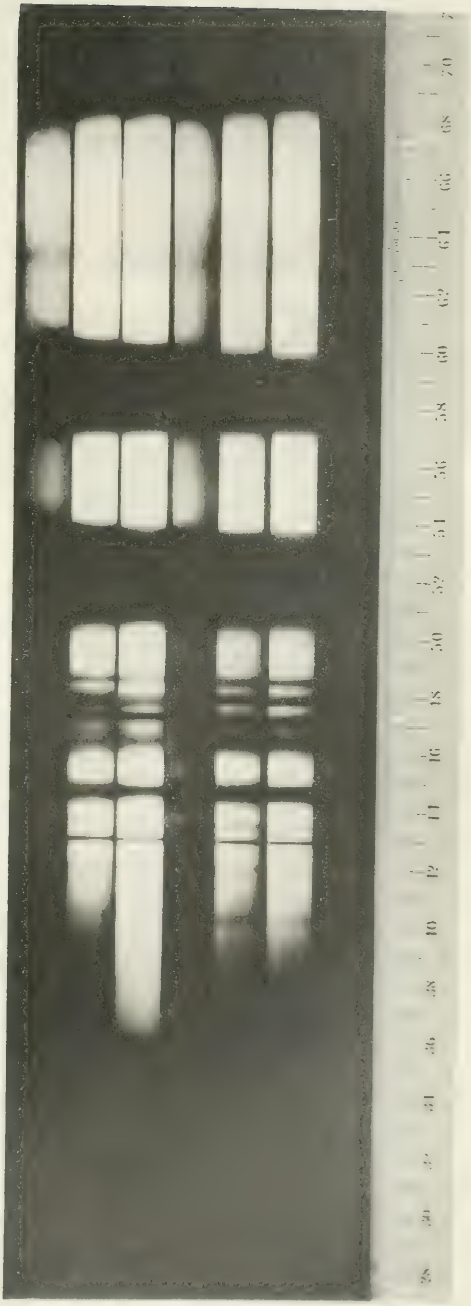
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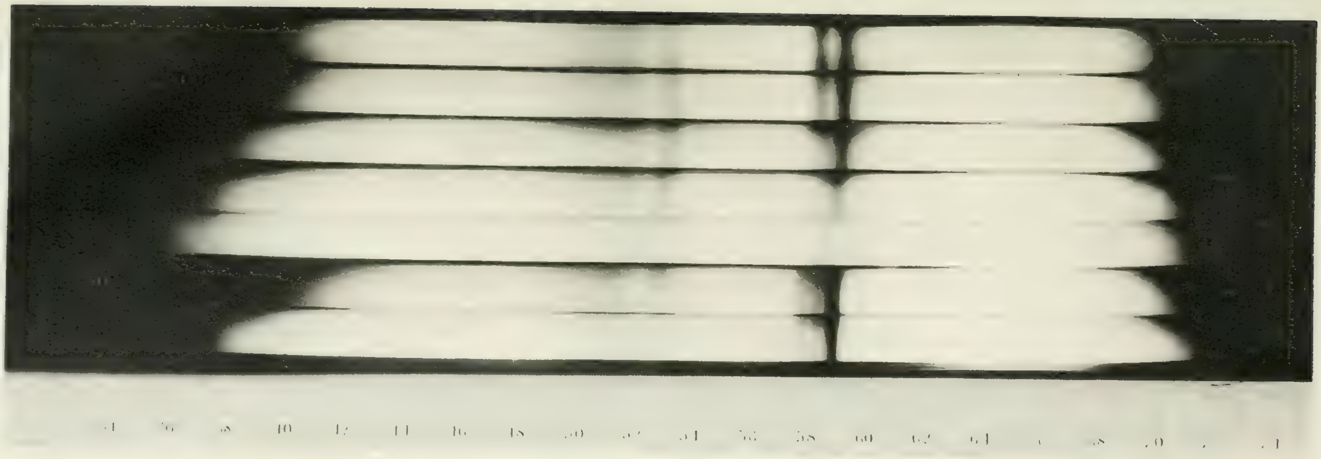
CAMPBELL ART CO., ELIZABETH, N. J.



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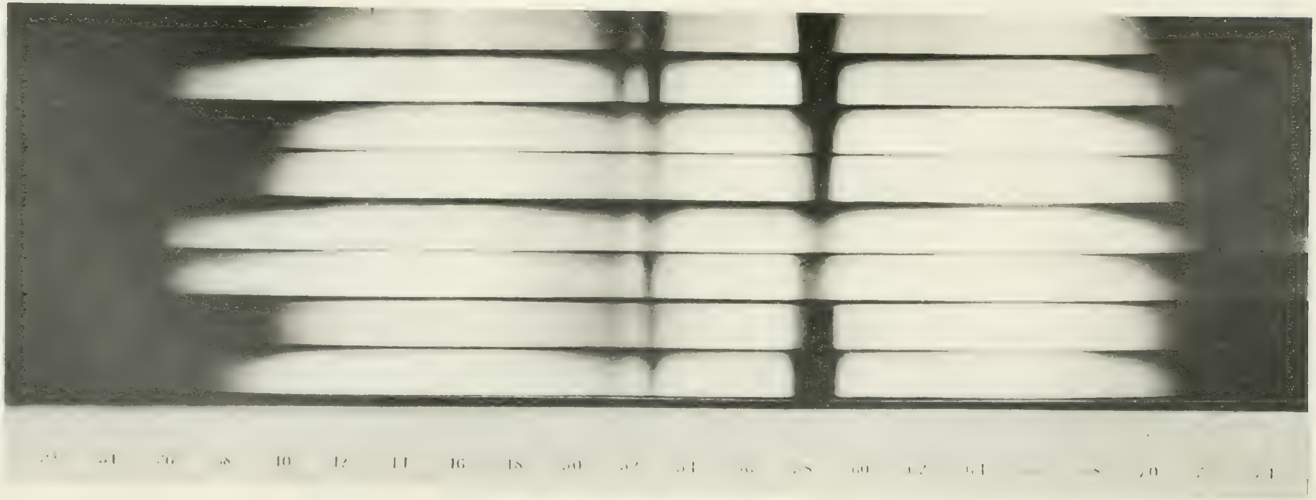

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CAMPBELL ART CO. ELIZABETH N. J.

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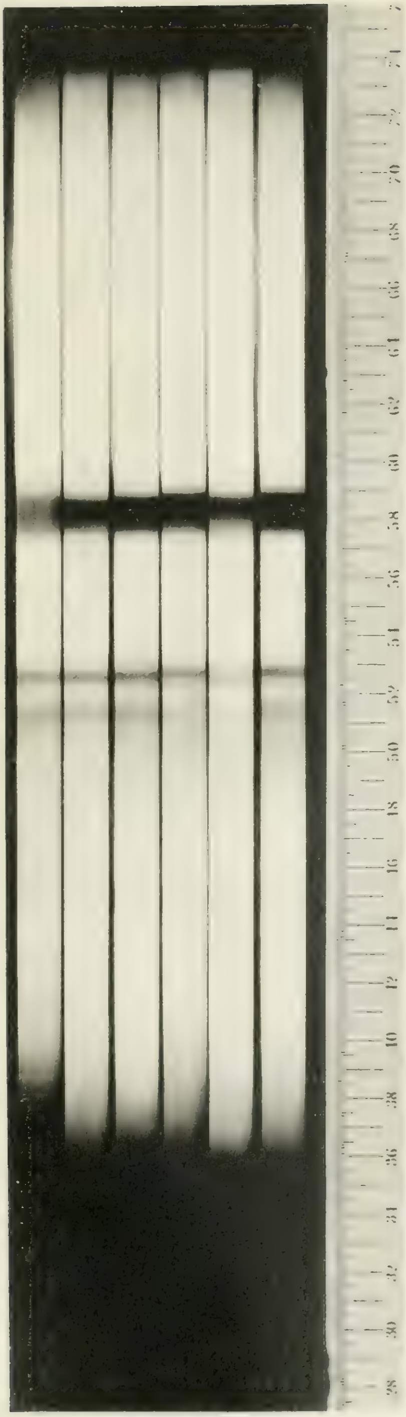
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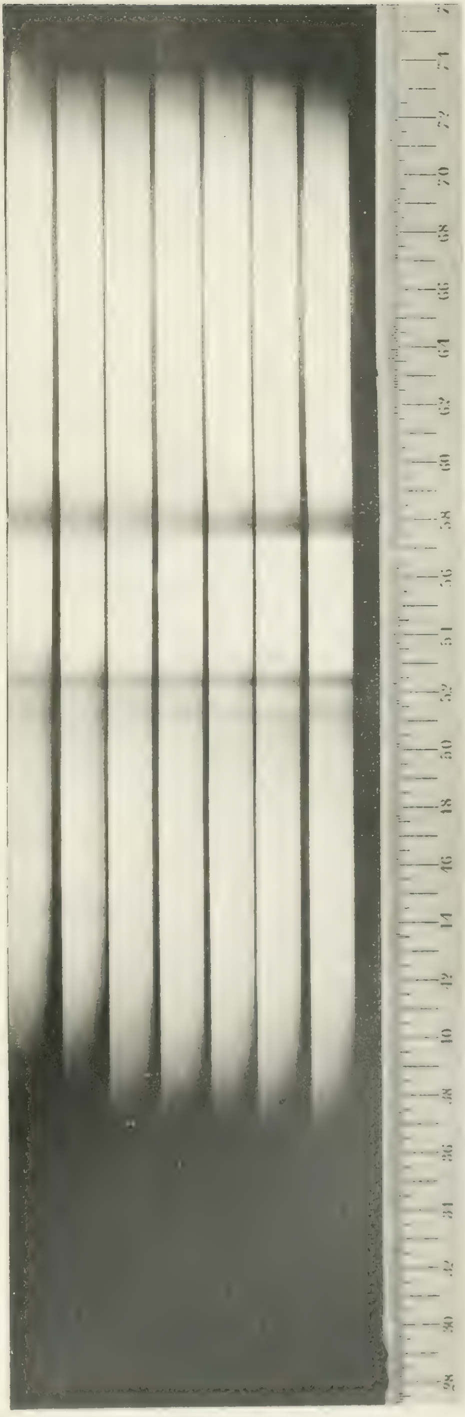
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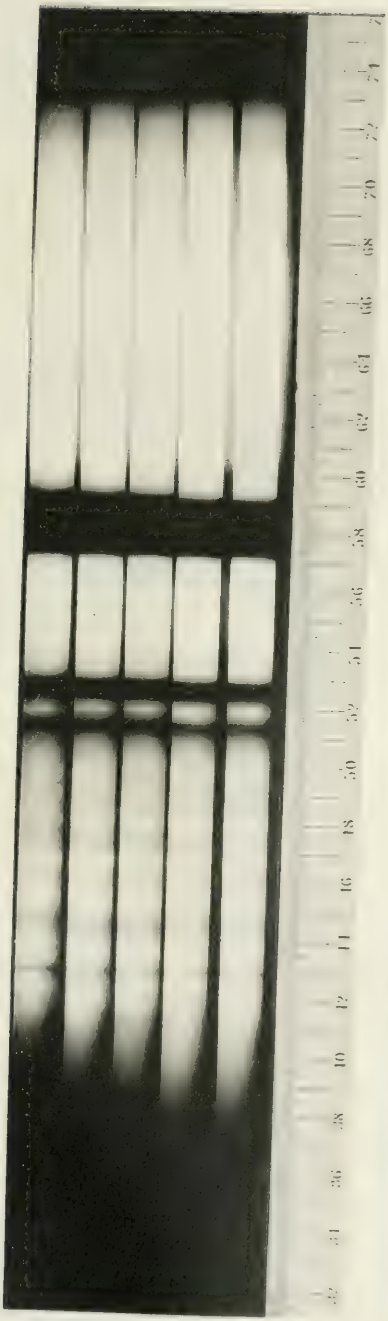
CAMPBELL ART CO., ELIZABETH, N. J.



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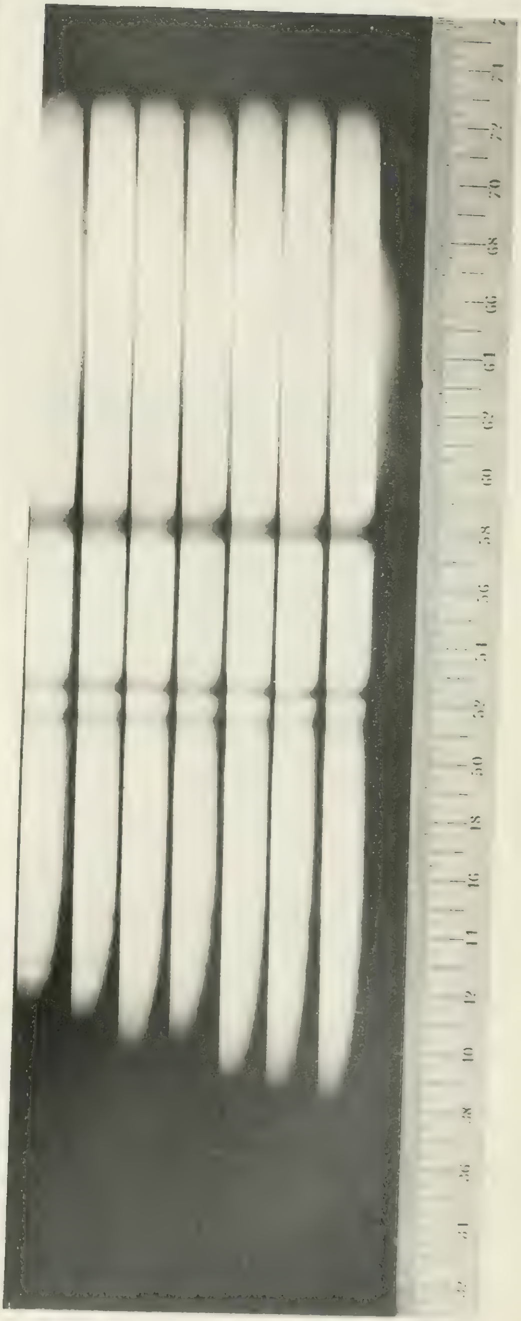

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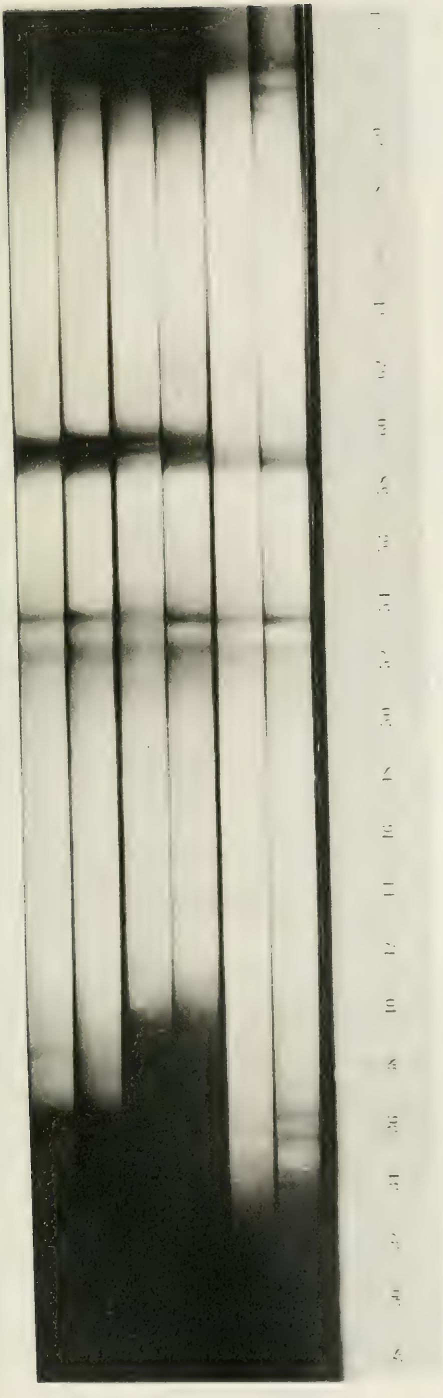

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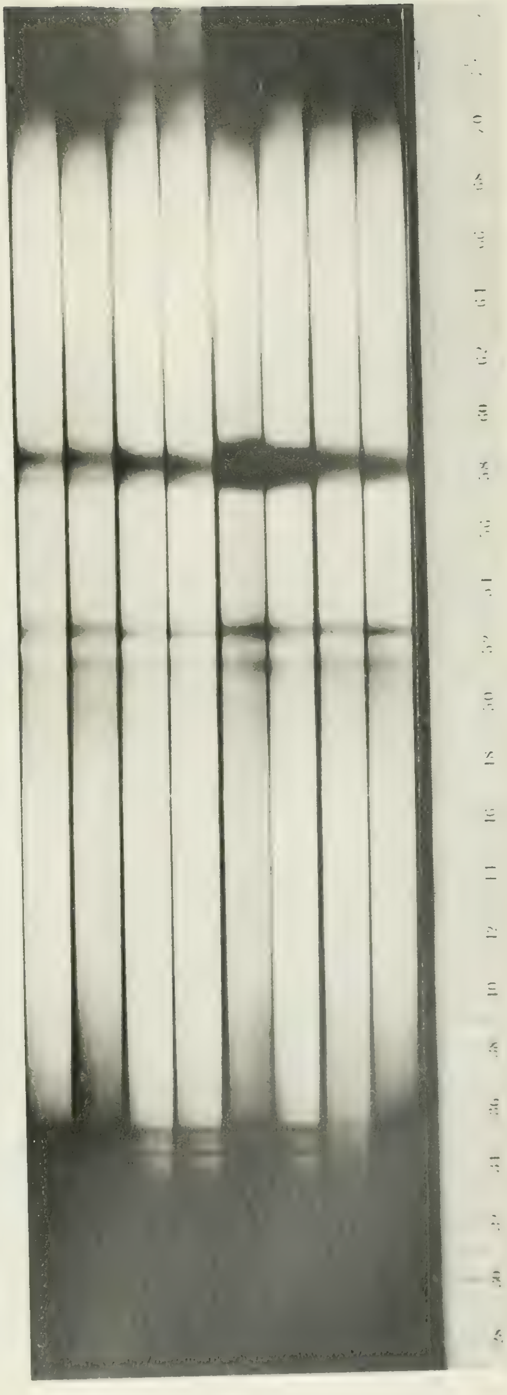

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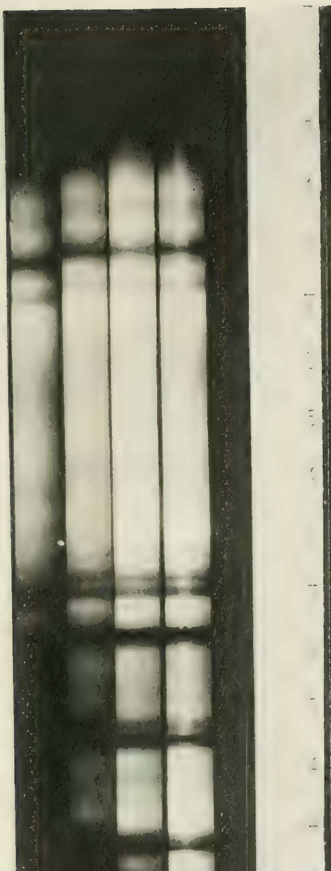
CAMPBELL ART CO., ELIZABETH, N. J.



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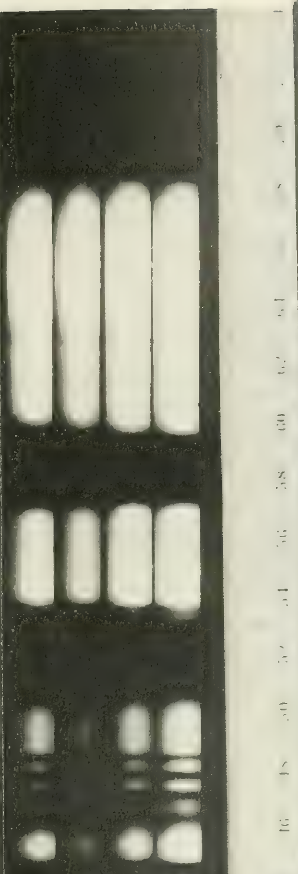

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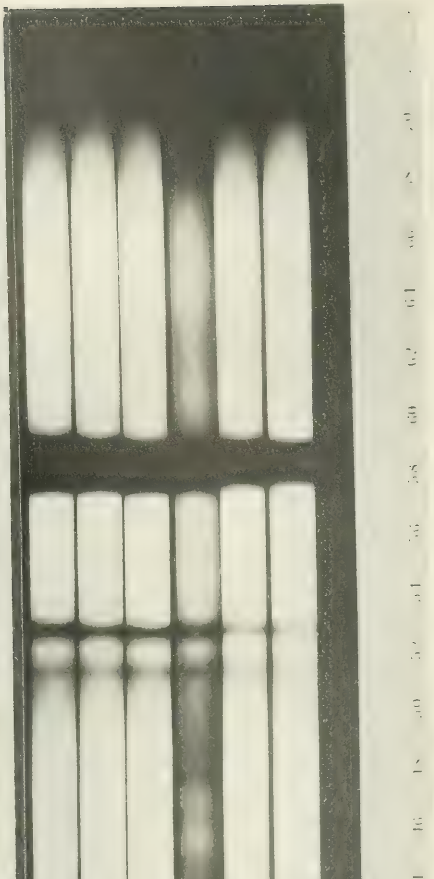

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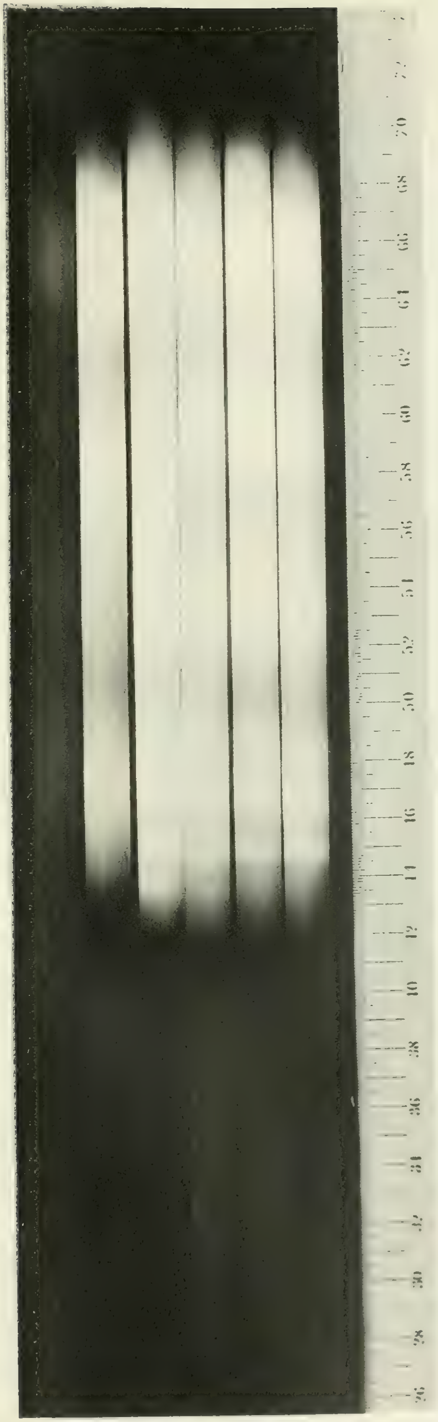
PBELL ART CO., ELIZABETH, N. J.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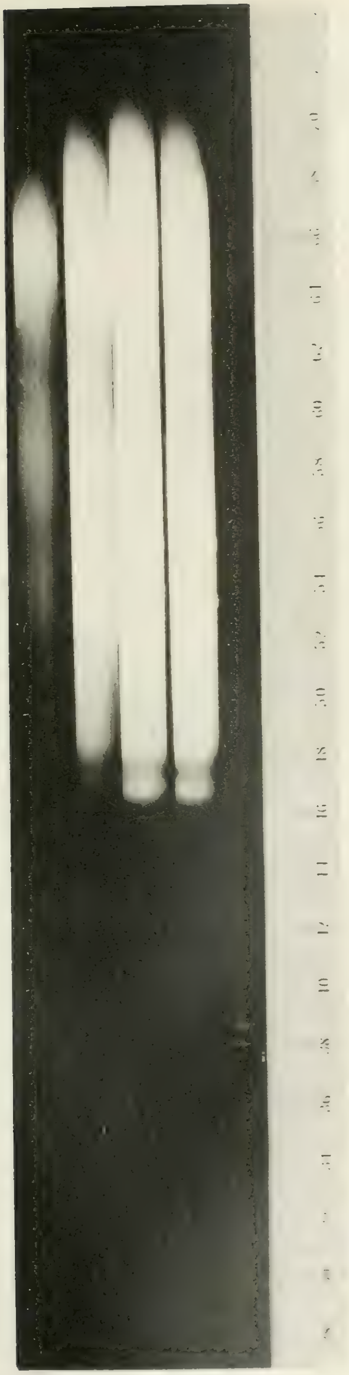

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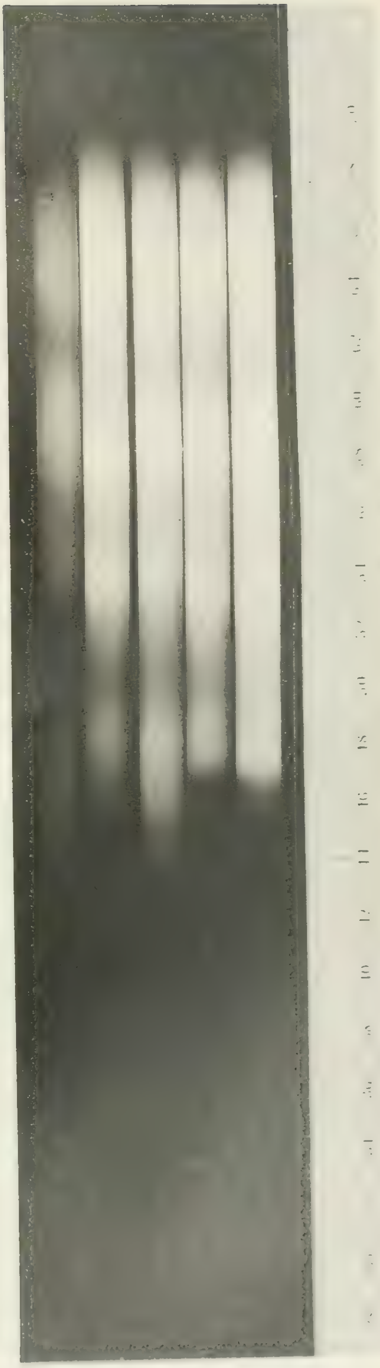

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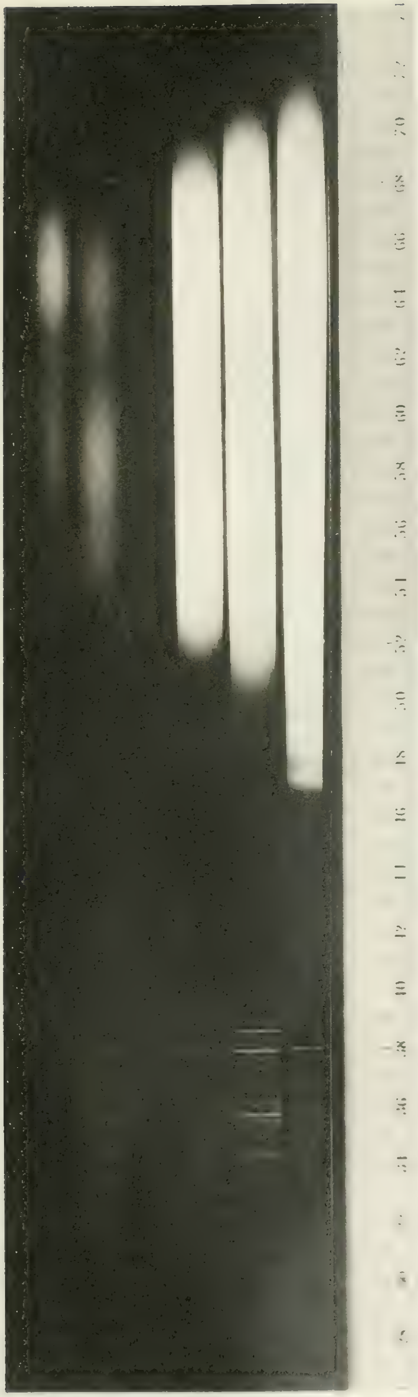
AMPRELL ART CO., ELIZABETH, N. J.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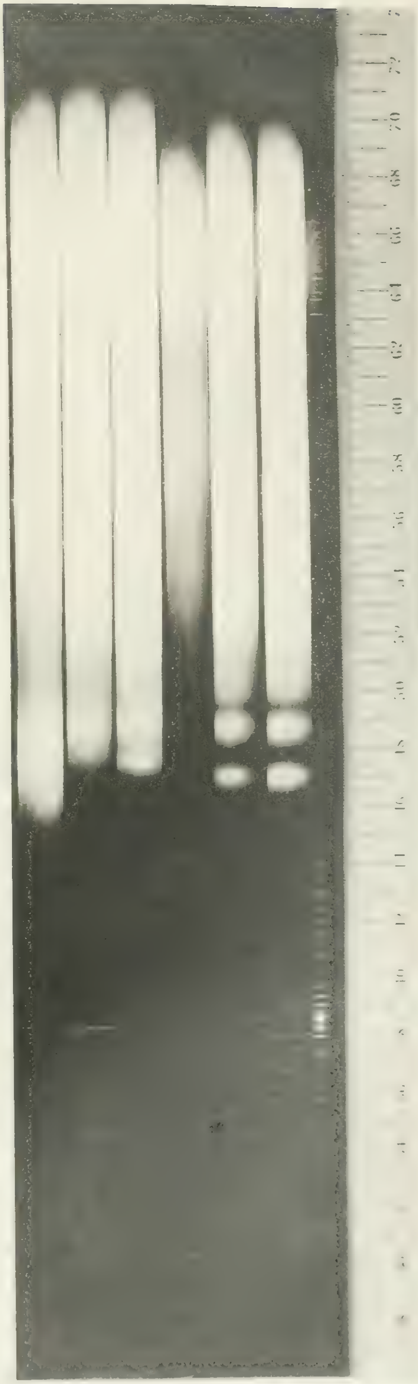
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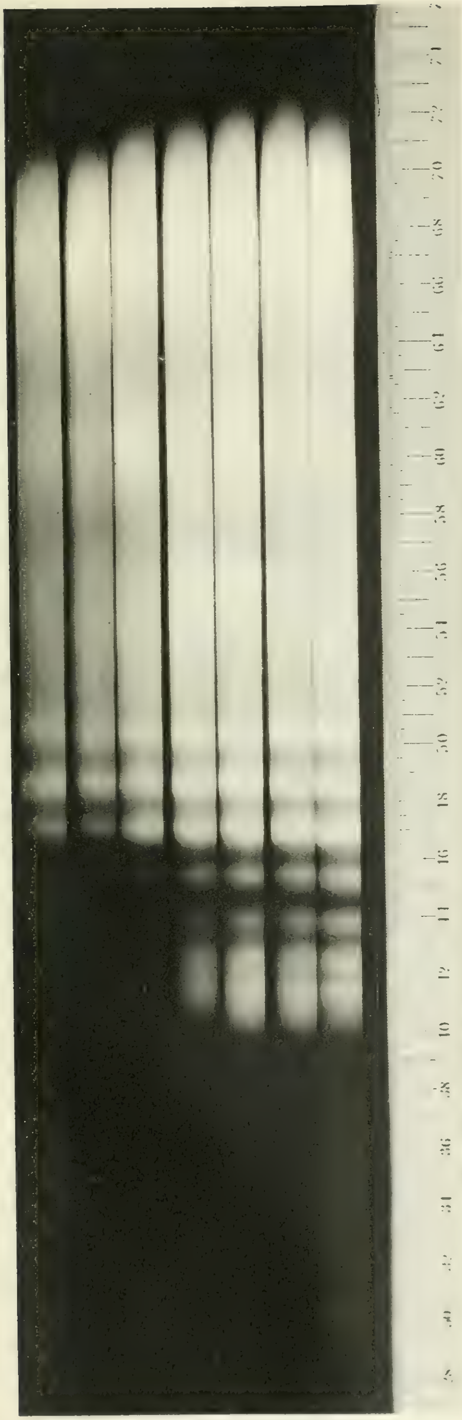
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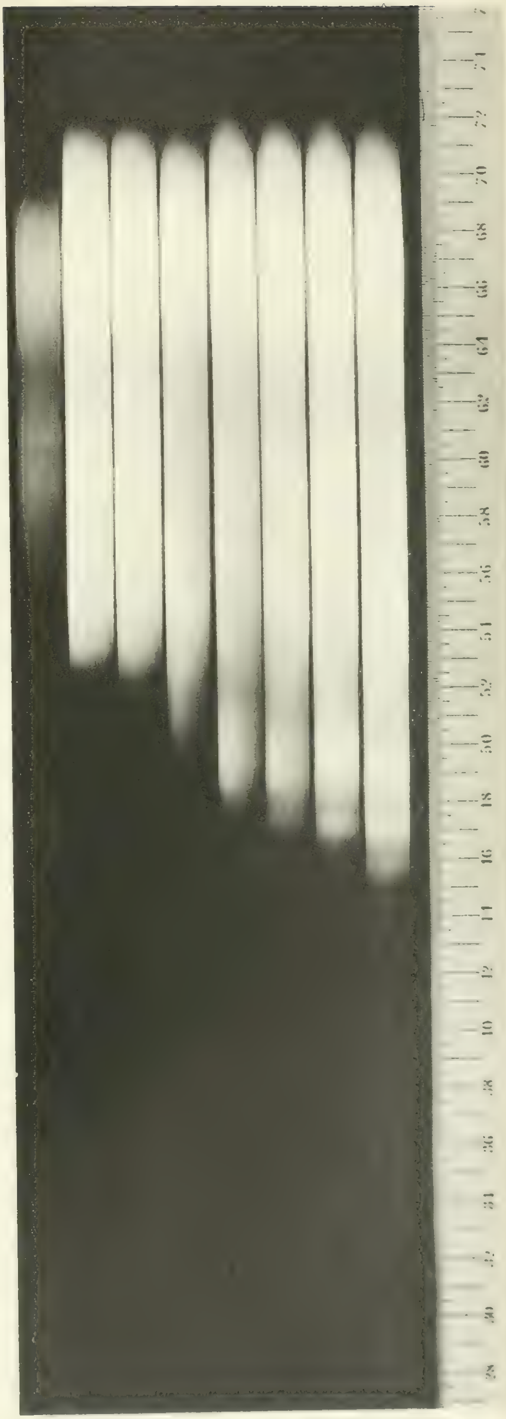
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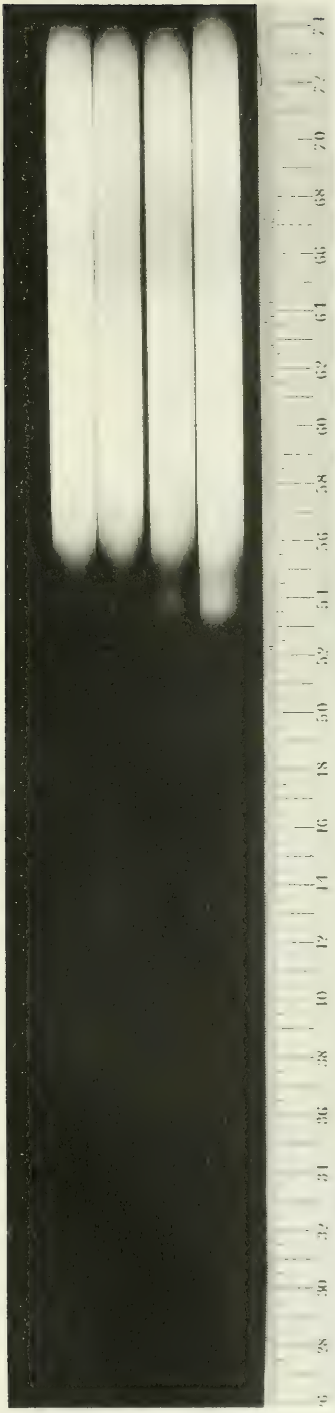
CAMPBELL ART CO., ELIZABETH, N. J.



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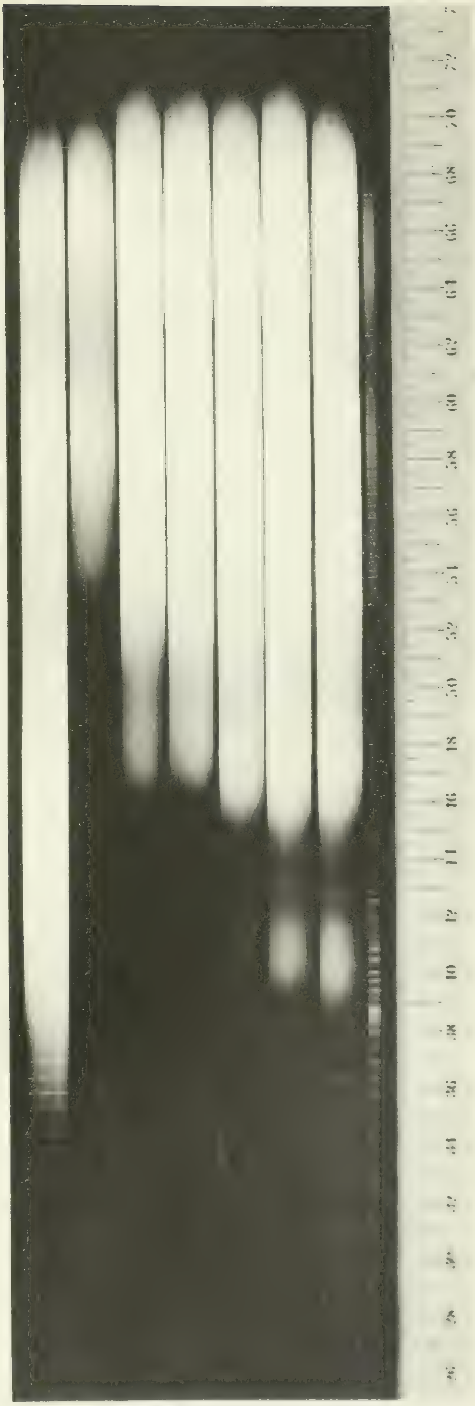

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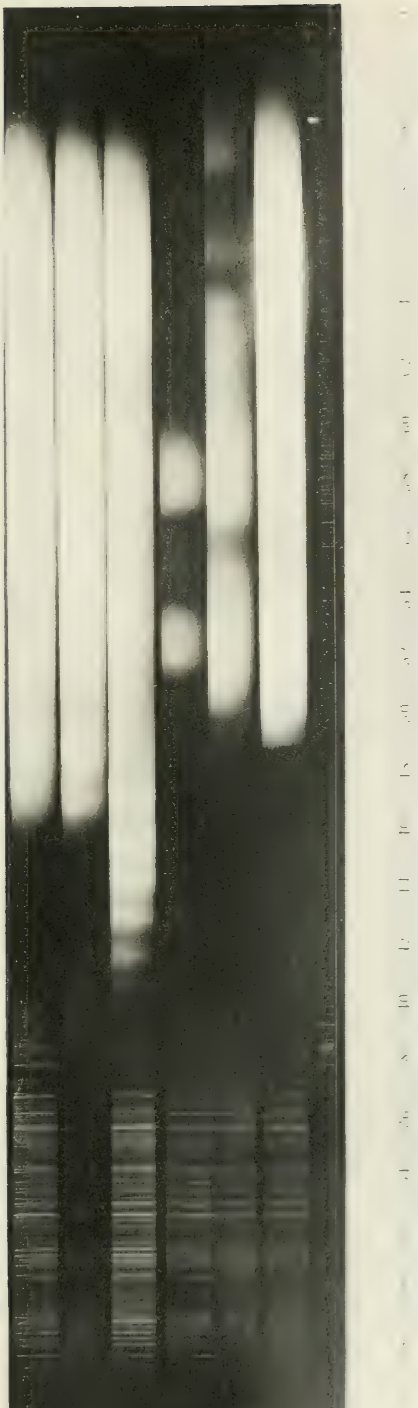

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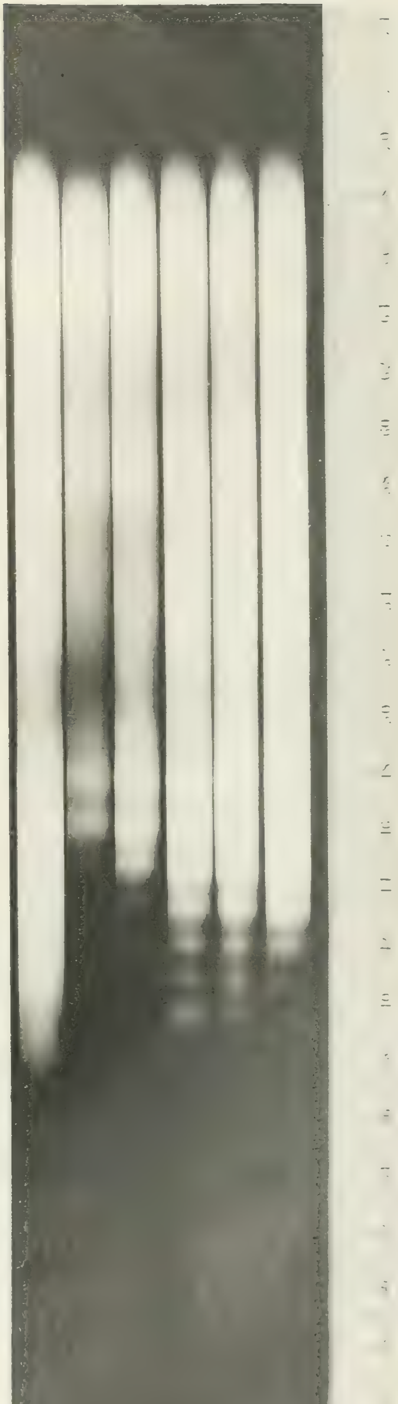

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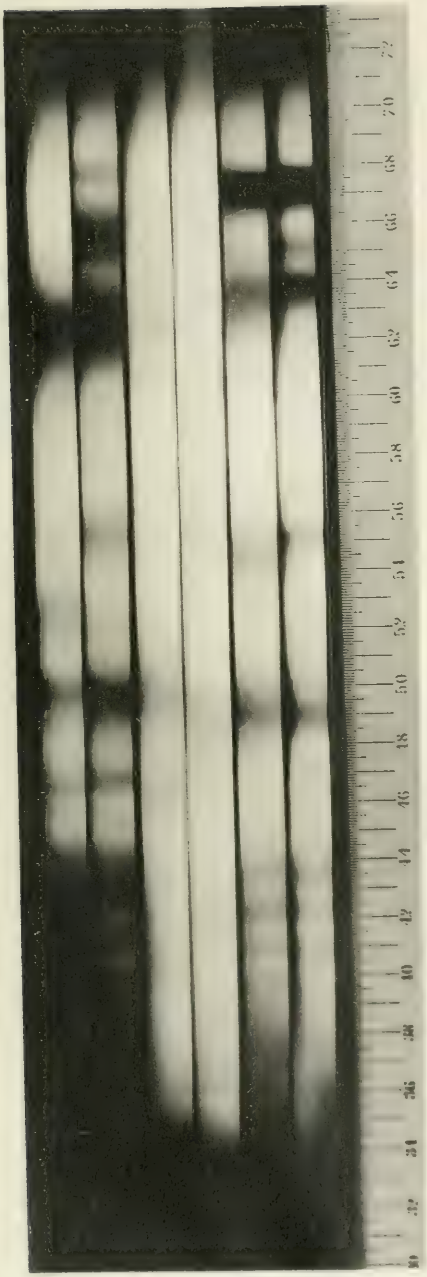
CAMERA ART CO. ELIZABETH, N. J.

PLATE 17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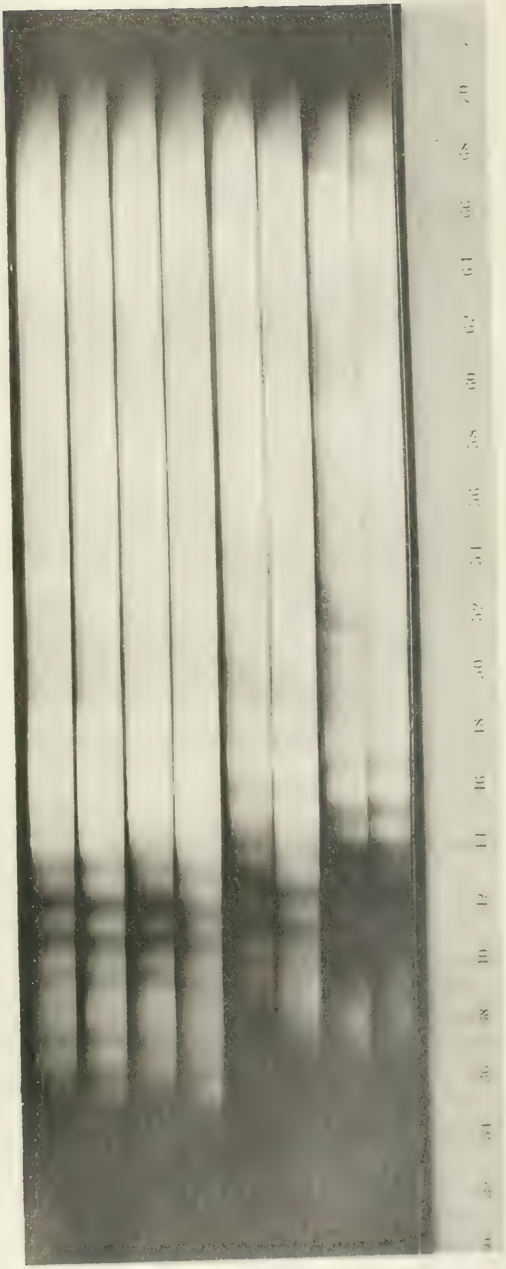

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